SILICON INVERSE OPAL-BASED MATERIALS AS ELECTRODES FOR LITHIUM-ION BATTERIES: SYNTHESIS, CHARACTERISATION AND ELECTROCHEMICAL PERFORMANCE

By

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A thesis submitted in conformity with the requirements for the degree of

Doctor of Philosophy

Department of Chemistry

University of Toronto

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Silicon Inverse Opal-Based Materials as Electrodes for
Lithium-Ion Batteries: Synthesis, Characterisation and
Electrochemical Performance

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Abstract

Three-dimensional macroporous structures (‘opals’ and ‘inverse opals’) can be produced by colloidal crystal templating, one of the most intensively studied areas in materials science today. There are several potential advantages of lithium-ion battery electrodes based on inverse opal structures. High electrode surface, easier electrolyte access to the bulk of electrode and reduced lithium diffusion lengths allow higher discharge rates. Highly open structures provide for better mechanical stability to volume swings during cycling.

Silicon is one of the most promising anode materials for lithium-ion batteries. Its theoretical capacity exceeds capacities of all other materials besides metallic lithium. Silicon is abundant, cheap, and its use would allow for incorporation of microbattery production into the semiconductor manufacturing. Performance of silicon is restricted mainly by large volume changes during cycling.
The objective of this work was to investigate how the inverse opal structures influence the performance of silicon electrodes. Several types of silicon-based inverse opal films were synthesised, and their electrochemical performance was studied.

Amorphous silicon inverse opals were fabricated via chemical vapour deposition and characterised by various techniques. Galvanostatic cycling of these materials confirmed the feasibility of the approach taken, since the electrodes demonstrated high capacities and decent capacity retentions. The rate performance of amorphous silicon inverse opals was unsatisfactory due to low conductivity of silicon. The conductivity of silicon inverse opals was improved by crystallisation. Nanocrystalline silicon inverse opals demonstrated much better rate capabilities, but the capacities faded to zero after several cycles.

Silicon-carbon composite inverse opal materials were synthesised by depositing a thin layer of carbon via pyrolysis of a sucrose-based precursor onto the silicon inverse opals in an attempt to further increase conductivity and achieve mechanical stabilisation of the structures. The amount of carbon deposited proved to be insufficient to stabilise the structures, and silicon-carbon composites demonstrated unsatisfactory electrochemical behaviour.

Carbon inverse opals were coated with amorphous silicon producing another type of macroporous composites. These electrodes demonstrated significant improvement both in capacity retentions and in rate capabilities. The inner carbon matrix not only increased the material conductivity, but also resulted in lower silicon pulverisation during cycling.
Памяти мамы...
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List of Abbreviations

3D  three-dimensional
ALD  atomic layer deposition
a-Si:H  hydrogenated amorphous silicon
CCD  charge-coupled device
CV  cycling voltammetry
CVD  chemical vapour deposition
CVI  chemical vapour infiltration
DC  direct current
DEC  diethyl carbonate
DMC  dimethyl carbonate
EC  ethylene carbonate
EDX  energy dispersive X-ray spectroscopy
EISA  evaporation induced self-assembly
f.c.c.  face centre cubic
FWHM  full width at half maximum
h.c.p  hexagonal close-packed
HRTEM  high-resolution transmission electron microscopy
ICP  inductively coupled plasma
IHEISA  isothermal heating evaporation induced self-assembly
LiPON  lithium phosphorous oxynitride
NADH  nicotinamide adenine dinucleotide plus hydrogen
Nd:YAG  neodymium yttrium aluminium garnet
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBN</td>
<td>pyrolytic boron nitride</td>
</tr>
<tr>
<td>PDDA</td>
<td>poly(diallyldimethylammonium chloride)</td>
</tr>
<tr>
<td>PDMS</td>
<td>polydimethylsiloxane</td>
</tr>
<tr>
<td>PEO</td>
<td>polyethylene oxide</td>
</tr>
<tr>
<td>PMMA</td>
<td>poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PPO</td>
<td>polyphenylene oxide</td>
</tr>
<tr>
<td>PSS</td>
<td>poly(4-styrenesulfonate sodium)</td>
</tr>
<tr>
<td>PVdF</td>
<td>polyvinylidene fluoride</td>
</tr>
<tr>
<td>PVdF-HFP</td>
<td>poly(vinylidene-fluoride-co-hexafluoropropylene)</td>
</tr>
<tr>
<td>PXRD</td>
<td>powder X-ray diffraction</td>
</tr>
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<td>RIE</td>
<td>reactive ion etching</td>
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<td>solid-electrolyte interphase</td>
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<td>TAL</td>
<td>titanium(IV) bis(ammonium lactato) dihydroxyde</td>
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<td>TGA</td>
<td>thermogravimetric analysis</td>
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<td>XRD</td>
<td>(powder) X-ray diffraction</td>
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<tr>
<td>μ-Raman</td>
<td>Raman micro-spectroscopy</td>
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CHAPTER 1.

INTRODUCTION. ARTIFICIAL OPALES: FROM

PHOTONICS TO LITHIUM-ION BATTERIES

1.1. Colloidal Crystals as Materials for Photonics and Beyond

Three dimensional arrays of colloidal particles have generated intense interest, mainly due to their possible applications in photonics. The special optical properties of such materials arise as a consequence of the periodic change in refractive index on the sub-micron length scale. These materials are usually referred to as colloidal crystals or as (artificial) opals because they mimic the structure and iridescence of natural opals (Figure 1.1). Natural precious opals consist of an array of close-packed silica microspheres that are arranged in a face centre cubic lattice [1]. Artificial opals are most often fabricated from polymer or silica monodisperse spheres. In comparison with other types of photonic crystals, colloidal crystals possess the large advantage that they allow for a facile low-cost and large-area preparation.
A new synthetic paradigm appeared in the late 1990s when it has been recognised that colloidal crystals could be utilised as templates for the preparation of three-dimensionally ordered porous replicas, so called ‘inverse opals’, as shown in Figure 1.2. After opal assembly, the voids between spheres are filled with the desired material, followed by removal of the template using chemical etching, solvent extraction or thermal treatment. The resulting inverse of the colloidal crystal is an interconnected periodic arrangement of air spheres within a matrix of the originally infiltrated material. Following the original work by Velev et al. [2], where macroporous silica was templated by a colloidal crystal film of surfactant modified polystyrene latex spheres, a wide variety of macroporous structures based on colloidal crystal templating have been synthesised, including polymers [3], ceramics [4], metals [5], semiconductors [6] and carbons [7].
In recent years it has become widely recognised that inverse opal architectures may benefit a wide range of applications beyond the field of photonic crystals. The nanoscale structure of the inverse opal skeleton provides a large surface area, short diffusion lengths, easy access and fast transport of reagents inside the porous structure. Some applications utilise the benefits of the high surface open structure of an inverse opal, others rely on the combination of its unique optical properties and macroporosity. The ‘non-photonic’ applications of inverse colloidal crystals include such diverse fields as chemical and biological sensing based either on optical changes [8], changes in conductivity [9], or electrochemical response [10] upon an analyte’s infiltration in the pores or its adsorption on the walls; simultaneous chromatographic separation and optical sensing [11,12]; biomedical research [13,14]; catalysis [15,16]; power storage and generation [17,18].
1.2. Lithium-Ion Batteries as Advanced Power Sources

Nowadays the demand for light-weight electric power sources that can provide high energy and high power density is probably higher than ever before due to the exponential growth in the number of portable electronic devices and cordless tools, and to increasing interest in electric and hybrid powered vehicles. Since lithium-ion cells were introduced to the market by Sony in the early 1990s they have become the dominant battery type for many of these applications [19]. Lithium-ion batteries offer specific energies higher than other electrochemical power sources due to high electrode capacities and operating voltages of up to ~5 V. The technology of lithium-ion batteries is still a relatively young and fast growing field, and it is apparent that significant improvements in lithium-ion battery performance are on the near horizon. These improvements will probably be achieved through the introduction of new battery materials and through the employment of new material architectures.

1.3. Outline of Thesis

This work was inspired by a desire to apply extensive expertise in the field of photonic crystals and in fabrication of inverse opals in particular that has been developed and accumulated by gifted researchers in my supervisors group, to the development of new battery materials.

The goal of my Ph.D. research was to develop new lithium-ion battery electrode materials based on inverse opal architectures. Silicon inverse colloidal crystal seemed to be a nearly perfect candidate for a new generation lithium-ion cell electrode, as it combines huge capacity of silicon, short lithium diffusion paths and relatively high
surface area to increase current rates, with high porosity to accommodate material volume changes during lithium insertion.

Several materials, namely amorphous hydrogenated silicon, nano-crystalline silicon, hard carbon, nano-crystalline silicon – carbon composites and carbon – amorphous silicon composite, were synthesised in the form of inverse opal films. Electrochemical properties of the above films of various thicknesses templated from silica opals of different sphere sizes were systematically studied. High capacity values and decent cycling performance of the amorphous silicon inverse opals confirmed that macroporous structures indeed allow reduction of mechanical stresses caused by material volume swings. However, the performance of amorphous silicon inverse opal films at higher current rates was unsatisfactory due to low electrical conductivity of the material. This problem was significantly mitigated by synthesising an inverse opal composite material in which conductive carbon backbone was coated with amorphous silicon. Electrodes made of such composites demonstrated high capacities, very good capacity retentions and excellent rate capabilities.

This thesis is organised so that synthetic procedures and characterisation of as-synthesised materials are described first, followed by the discussion of electrochemical performance of these materials. Chapter 2 will be devoted to the brief description of battery working principles and to the important characteristics of battery materials. Advantages and drawbacks of nanostructured electrode materials and of inverse opals in particular will be discussed in Chapter 3. Techniques used in study for physico-chemical and electrochemical material characterisation will be described in Chapter 4. And Chapter 5 will examine the synthesis of monodisperse silica colloidal particles and
preparation of colloidal crystal templates. In Chapter 6, the synthesis and electrochemical characterisation of silicon inverse opals will be presented. Properties of different carbon types will be discussed in Chapter 7 followed by a description of carbon inverse colloidal crystals synthesis and their electrochemical characterisation. A brief review of composite materials based on inverse opal structures will be given in Chapter 8, synthetic procedures used to make silicon-carbon and carbon-silicon composites will be described and their electrochemical performance will be discussed. Finally, conclusions will be given in Chapter 9 and perspectives and future directions of the research will be outlined.

1.4. References


CHAPTER 2.

LITHIUM-ION BATTERIES: CONCEPTS, CHARACTERISTICS AND DESIGN

2.1. Preamble

Batteries have long taken an important place in our everyday lives. An average family in North America uses around 50 batteries in the household and in personal items. Advancements in electronic technology and in other fields, such as electric vehicles, necessitate development of new rechargeable batteries capable of delivering higher power per mass unit. Lithium batteries have become the device of choice for high power applications because they offer both the highest energy density and specific energy (Figure 2.1).

![Energy storage capability of various battery systems.](image)

Figure 2.1.

Energy storage capability of various battery systems.
In this chapter I discuss the fundamental concepts and principles of battery operation, review the most commonly used ones, as well as promising electrode materials for lithium-ion batteries, with a particular emphasis on carbonaceous and silicon-based anode materials.

2.2. Basic Battery Concepts

2.2.1. Principles of operation

A battery, strictly speaking, is a device composed of two or more electrochemical cells connected in series, parallel, or both, according to the required output voltage and capacity. The term ‘battery’, however, has evolved to mean an electrochemical powering device, regardless of the number of cells it contains. In this thesis terms ‘battery’ and ‘cell’ are used interchangeably.

An electrochemical cell converts the chemical energy stored in it into electrical energy by virtue of red-ox reactions occurring at its electrodes. If these reactions are irreversible the cell is termed primary, whereas rechargeable or secondary cells utilise reversible reactions and thus can be cycled by applying external voltage. A principal scheme of a secondary battery is shown in Figure 2.2.
A battery comprises three main active components:

- **Negative electrode.** This is the place where a chemical compound undergoes an electrochemical oxidation during cell discharge. As indicated in Figure 2.2.a, electrons released in the oxidation reaction move through the external cell circuit to the opposite electrode. During cell charging the reverse reaction is happening (Figure 2.2.b) and reduction occurs.

- **Positive electrode.** Electrons from the negative electrode give rise to an electrochemical reduction as the cell discharges. The corresponding oxidation occurs during battery charge.

- **Electrolyte** allows motion of ions towards electrodes, so closing the circuit. The electrolyte is usually a solution of salts, alkalis or acids, but polymeric or solid electrolytes may also be used.

During cell discharge the term ‘anode’ can be used for the negative electrode, and ‘cathode’ for the positive electrode. The terminology should, in principle, be reversed.
during battery charging, however it has become customary among battery specialists to use ‘anode’ to refer to a negative electrode, and ‘cathode’ to refer to a positive electrode regardless of the direction of the electrochemical reaction. Following this nomenclature the terms ‘anode’ and ‘negative electrode’, ‘cathode’ and ‘positive electrode’ are considered synonymous and are used interchangeably throughout this thesis.

The criteria of practical electrode material selection for batteries are rather stringent, thus excluding potentially appealing anode-cathode couples. A good electrode material should meet most or all of the following requirements:

- High potential for cathode and low potential for anode;
- Limited potential variation during cell discharge;
- Low weight, thus providing high gravimetric capacity (Ah/kg);
- High density, giving high volumetric capacity (Ah/L);
- Capability of sustaining appreciable currents (this includes good electronic conductivity and, for insertion electrodes, fast ion diffusion);
- Chemical stability towards the other battery components;
- Low cost;
- Safety;
- Low toxicity.

Electrolyte is another term that is traditionally understood in the battery research differently than in other fields. A battery electrolyte can be defined as an ionic conductor that provides the medium for transfer of ions inside the cell between anode and cathode, i.e. in case of a typical liquid electrolyte the term refers not only to the salt, but to the salt and the solvent.
A sustainable battery technology requires a robust electrolyte that can provide stable cycling of the cell. Such an electrolyte should meet the following requirements:

- High ionic conductivity;
- Very low electronic conductivity in order to avoid battery self-discharge;
- Minimised reactivity to the electrode materials and other components of the cell;
- Thermodynamic, or at least kinetic, stability to decomposition in the cell operational voltage window;
- Physical and chemical stability at the operational and storage temperatures;
- Safety (e.g. high flash point);
- Low toxicity;
- Low cost.

2.2.2. Some important definitions

2.2.2.1. Cell voltage

The theoretical voltage of an electrochemical cell $E_{OC}$, or open circuit voltage, depends on the thermodynamic properties of electrode materials and can, in the first approximation, be defined as:

$$E_{OC} = \varphi_c - \varphi_a \quad \text{Eq. 2.1,}$$

where $\varphi_c$ and $\varphi_a$ are electrochemical potentials of cathode and anode respectively.

However, when connected to an external load, the operating voltage of the cell $E_d$ is always lower than $E_{OC}$ value due to ohmic losses and polarisation losses at the electrodes:

$$E_d = E_{OC} - (\eta_{act}^{(c)} + \eta_{conc}^{(c)}) - (\eta_{act}^{(a)} + \eta_{conc}^{(a)}) - iR \quad \text{Eq. 2.2,}$$
where $\eta^{(c)}_{act}$ and $\eta^{(a)}_{act}$ are activation polarisations, or charge transfer overvoltages at the cathode and anode respectively, $\eta^{(c)}_{conc}$ and $\eta^{(a)}_{conc}$ are concentration polarisations related to accumulation or depletion of electroactive species near the electrodes due to slow diffusion, $i$ is the operating current and $R_i$ is the internal resistance of the cell. Polarisation values are not constant, but increase with increasing operating current.

Conversely, voltages higher then $E_{OC}$ are required to charge the battery:

$$E_c = E_{OC} + \left( \eta^{(c)}_{act} + \eta^{(c)}_{conc} \right) + \left( \eta^{(a)}_{act} + \eta^{(a)}_{conc} \right) + iR_i$$  \hspace{1cm} \text{Eq. 2.3.}$$

2.2.2. Capacity

The electrochemical capacity $C$ of a cell is defined as the total quantity of electricity involved in the electrochemical reaction:

$$C = \int_{0}^{t} idt$$  \hspace{1cm} \text{Eq. 2.4.}$$

In the case of galvanostatic process Equation 2.4 can be rewritten as:

$$C = it$$  \hspace{1cm} \text{Eq. 2.5.}$$

Capacity is expressed in coulombs or, more often, in ampere-hours (1 Ah = 3600 C).

Each electrode has a nominal (or theoretical) capacity that is determined by the nature and amount of the active material. The specific capacity of a battery electrode $C_{electrode}$, usually expressed in mAh/g, can be calculated from the current $i$, the mass of the active electrode material $M$, and the elapsed time $t$:

$$C_{electrode} = \frac{it}{M}$$  \hspace{1cm} \text{Eq. 2.6.}$$
2.2.2.3. **C rate**

The ‘C rate’ is the rate at which the cell is cycled, expressed as a multiple of the nominal capacity; *i.e.* if the nominal capacity is discharged or charged in 1 hour then the rate is defined as 1C, in the case of 2 hour discharge it is termed C/2, and for a discharge in 6 minutes discharge rate equals 10C.

2.2.2.4. **Specific energy and energy density**

Specific energy is defined as the total amount of energy stored per unit weight and is expressed as the product of operating voltage and capacity. It is expressed as in watt-hours per kilogram, Wh/kg. The volumetric energy density is expressed in watt-hours per litre, Wh/L.

Both output voltage and capacity should be maximised to improve the energy storage. A secondary battery with light weight and hence high specific energy is a major candidate for modern applications. Energy density is an important characteristic of miniature batteries and especially microbatteries, where size plays a more important role than weight of the cell.

2.3. **Lithium-Ion Batteries**

2.3.1. **Introduction**

Being the lightest metal (equivalent weight – 6.94 g/mol, density – 0.53 g/cm³) and one of the most electropositive elements (electronegativity by Pauling scale – 0.98) lithium was ‘destined’ to become a favourite object of battery research. The low atomic weight of lithium allows it to deliver very high energy density per electron transferred, while its low electronegativity promises high cell voltages. Metallic lithium was first employed as an anode electrode material for primary $\text{Li}/(CF)_n$ batteries in the late 1960s
by the Matsushita company [1]. Later, batteries based on intercalation positive electrodes, such as layered dichalcogenides titanium disulfide \(TiS_2\) and molybdenum disulfide \(MoS_2\) were developed, leading to the initiation of rechargeable lithium batteries [2,3]. Lithium-ion batteries based on graphitic anodes and metal oxide cathodes were successfully commercialised in the 1990s and have dominated the rechargeable batteries market ever since [4].

Lithium-ion batteries employ lithium intercalation or lithium insertion compounds both as the positive and negative electrode materials. As a battery is cycled, both lithium ions and corresponding electrons exchange between anode and cathode (Figure 2.3). These cells are also referred to as ‘rocking chair’ batteries as lithium ions ‘swing’ back and forth between electrodes as the cell is charged and discharged.

![Figure 2.3.](image)

Schematic representation of a lithium-ion ‘rocking chair’ battery during discharge.

Electrode and electrolyte materials employed in the state-of-the-art lithium-ion batteries, as well as the prospective electrode materials and possible material designs for next-generation batteries, are discussed in the following sections.
2.3.2. Electrolytes

For lithium-ion batteries use of any electrolytes that have active protons has to be ruled out, as none of them are stable against proton reduction at the active anode. Therefore, aprotic solvents that are polar enough to dissolve sufficient amounts of lithium salt have to be used in lithium-ion cells.

Five types of electrolytes can be used in lithium-ion batteries:

- liquid electrolytes,
- polymer-gel electrolytes,
- polymer electrolytes,
- ionic liquids,
- ceramic electrolytes.

Liquid electrolytes are solutions of a lithium salt in polar organic solvents. An overwhelming amount of research has been conducted to optimise composition of liquid electrolytes [5 and references therein]. Large number of solvents, including cyclic and linear carbonates, esters, ethers, and different salts, such as lithium perchlorate $\text{LiClO}_4$, lithium hexafluoroarsenate $\text{LiAsF}_6$, lithium tetrafluoroborate $\text{LiBF}_4$, lithium hexafluorophosphate $\text{LiPF}_6$, have been studied in the ‘quest for the ideal electrolyte’ that would be highly conductive, stable, non-toxic, environmentally friendly and cheap. So far, no such ideal had been found, but rather a ‘compromise’ formulation has been developed. Most state of the art batteries use $\text{LiPF}_6$ in a mixture of ethylene carbonate (EC) and one or more linear carbonates, usually dimethyl carbonate (DMC) and/or diethyl carbonate (DEC).
Polymer-gel electrolytes are based on polymers gelled by conventional liquid electrolytes. High molecular weight polymer, fully swollen by organic solvent, serves only to provide dimensional stability. Most commonly used polymer-gel electrolytes are based on poly(vinylidene-fluoride-co-hexafluoropropylene) (PVdF-HFP) and $LiPF_6$ in a solution of organic carbonates. An advantage of gel electrolytes is that the liquid is absorbed within the polymer, and is thus less likely to leak from a cell.

In polymer electrolytes high molecular weight polymers serve both as solvents to dissolve lithium salts and as matrices providing mechanical stability. These electrolytes are usually made of polyethylene oxide (PEO) or other ether-based polymers. Such electrolytes provide good mechanical strength and reasonable conductivities. However, their use is limited to low voltage batteries as these materials are unstable to oxidation on cathodes at voltages exceeding 3.5-4.0 V vs. $Li/Li^+$. 

Ionic liquids are a new promising class of electrolyte materials. They stay liquid in a wide temperature range, have low volatility, high decomposition temperatures and low flammability, and are stable in a wide voltage window. However, they still have not found their way to commercial cells mainly because of high viscosity, especially at room temperatures [6].

Inorganic ceramic electrolytes have been used in thin film solid-state batteries. This type of lithium-ion battery was developed for semi-conductor and printed circuit board applications. Thin film solid-state cells are viable as on-chip or on-board power sources for microelectronics. They are able to sustain high temperatures, and can be fabricated by high volume manufacturing techniques on silicon wafers. Different lithium
conductive materials, such as lithium phosphorous oxynitride (LiPON), can be used as electrolytes in these cells [7].

**2.3.3. Separators**

A comprehensive review of separators for lithium-ion batteries is given by Zhang [8]. Liquid electrolyte batteries require the use of a separator that is placed between the electrodes to prevent their physical contact while enabling free ionic transport. Although the separator itself does not participate in any reactions in the cell, its structure and properties affect such battery characteristics as the energy and power densities, cycle life and safety. The separator must be chemically and electrochemically stable towards the electrolyte and electrode materials and must be mechanically strong to withstand the high tension during the battery assembly. It should have sufficient porosity and wettability to absorb enough electrolyte for the high ionic conductivity. To ensure high energy densities the separator has to be as thin and porous as possible while still retaining mechanical strength. For safety reasons, separators are often made as multilayer materials, designed in such a way that one layer melts to close the pores below the thermal runaway temperature and shut down the battery operation, while the other layer provides mechanical strength to prevent physical contact of the electrodes. Battery separators can be divided into three types: microporous polymer membranes, non-woven fabric mats and inorganic composite membranes. Microporous polyolefin membranes based on polyethylene, polypropylene or blends of these two are the most widely used type due to their comprehensive advantages of performance, safety and cost.
2.3.4. Cathode materials

Probably most of the research related to lithium-ion batteries is devoted to cathode materials. Electrochemical characteristics of large number of compounds have been studied, including such materials as polymers, layered transition metal chalcogenides ($TiS_2$, $VSe_2$), layered transition metal oxides ($V_xO_3$), layered lithium-transition metal oxides ($LiNiO_2$, $LiCoO_2$), spinels ($LiMn_2O_4$), phosphates with olivine-like structures ($LiFePO_4$, $Li_3V_2(PO_4)_3$, $VOPO_4$). An excellent review of lithium battery cathode materials is given by Whittingham [9]. In this section I briefly discuss some of the most commercially important, as well as prospective positive electrode materials.

Layered lithiated nickel, cobalt and manganese oxides and their solid solutions are among the most extensively studied and widely used cathode materials for lithium batteries [10-12]. These materials, having a general formula of $LiMO_2$ ($M = Ni$, $Co$, $Mn$, or $Ni/Co/Mn$), are isostructural to $\alpha$-$NaFeO_2$. In this layered structure oxygen anions are arranged in a cubic close-packed lattice with the alternate layers between oxygen sheets occupied by transition metal. Lithium is inserted into the essentially empty remaining layers (Figure 2.4). $LiNiO_2$ and $LiCoO_2$ materials possess reasonable structural stability during cycling. Their solid solutions of the general formula $LiNi_{1-y}Co_yO_2$ are structurally even more stable than the end-member homologues and exhibit superior cycling performance [13]. However, limited resources and the high price of nickel and cobalt prevent extensive use of these materials. Solid solutions with manganese, such as $LiNi_{1-y}Mn_yO_2$, may find their use as high-rate electrodes in the future [14].
Figure 2.4.

Structure of layered lithiated transition metal oxides, $LiMO_2$ ($M = Ni, Co, Mn$). Lithium ions are shown between the transition metal/oxide sheets.

The lithium manganese spinel $LiMn_2O_4$ was originally proposed as a cathode material for lithium batteries by Thackeray et al [15]. The anion lattice containing cubic close-packed oxygen ions is in fact closely related to the $α-NaFeO_2$ structure, differing only in the distribution of the cations among the octahedral and tetrahedral sites (Figure 2.5). $LiMn_2O_4$ offers such advantages over $LiMO_4$ materials as lower cost, excellent rate capability, and minimal health and environmental impacts. However, the capacity of $LiMn_2O_4$ fades upon cycling, primarily due to the instability of $Mn^{3+}$ ion to disproportionation, especially at low voltages. Thusly produced $Mn^{2+}$ ions are soluble in acidic environment, so they are leached away in the presence of $HF$, which is usually present in trace amounts in $LiPF_6$-based electrolytes. Different approaches have been taken to eliminate this problem. Namely, $LiMn_2O_4$ can be protected by coating the spinel particles with such materials as zirconium dioxide $ZrO_2$ or aluminium phosphate $AlPO_4$. Substitution of small part of the manganese with aluminium stabilises the structure against reaction with acid. Alternatively, a fluoride-free electrolyte can be used.
Lithium intercalation into vanadium pentoxide has been the subject of study for more than 30 years [16]. $V_2O_5$ has a layered structure with weak vanadium-oxygen bonds between the layers (Figure 2.6). Vanadium oxides with mixed-valent metal ions, such as $V_6O_{13}$ and $LiV_3O_8$ have also been studied [17,18]. Vanadium oxides generally show large capacities, high voltages and good rate capabilities for lithium intercalation. However, they tend to become amorphous upon cycling, which limits their commercial use.

Figure 2.5.
Structure of cubic spinel $LiMn_2O_4$. Lithium ions are shown between the transition metal/oxide octahedrals.

Figure 2.6.
Structure of $V_2O_5$, showing the square pyramids sharing edges of the basal planes.
The emphasis of cathode research drastically changed in 1997 when Goodenough and colleagues demonstrated electrochemical extraction of lithium from $LiFePO_4$ [19]. This became the first truly environmentally benign and low cost potential cathode material. $LiFePO_4$ is isostructural to olivine $(Mg,Fe)_2SiO_4$ (Figure 2.7). This material has a very flat discharge plateau at $\sim 3.4 \text{ V vs. } Li/Li^+$ and a high reversible capacity comparable to that of $LiNiO_2$. However, its electrical conductivity is low which somewhat limits its use in high power applications, while the energy density is too small to compete in energy dense applications.

![Figure 2.7.](image)

The olivine-type structure of $LiFePO_4$.

### 2.3.5. Anode materials

Lithium metal should be the best negative electrode material for a rechargeable lithium battery in terms of its specific capacity and voltage profile. Nevertheless, safety considerations and lithium dendrite formation during repeated cycling, which eventually lead to internal short-circuiting, limit the use of metallic lithium in secondary batteries.
Research activity in this area has increased significantly in recent years – the number of publications grew almost 5-fold in the last 10 years, from 111 in year 1997 to 507 in 2007 [20]. A variety of materials have been suggested and used as alternatives to lithium anodes. Carbon, as the most widely used, and silicon, as one of the most promising new anode materials, are briefly reviewed in this section.

### 2.3.5.1. Carbonaceous materials

In terms of practical utility carbons these days are well ahead of all other anode materials for lithium-ion batteries. Lithium insertion in graphite host lattices from non-aqueous solvents was first reported as early as 1976 [21]. It was Sony Corporation in early 1990s who introduced to the market the first successful carbon-based lithium-ion batteries [22].

Carbons capable of lithium intercalation can be broadly divided into types [23]:

- graphitic carbons and
- non-graphitic carbons.

Both of these types can be employed as anode materials for lithium-ion batteries, however, specific capacities and voltage profiles depend greatly on the carbon type and preparation conditions.

Graphites have a layered structure formed by stacking of the planar graphene layers. Graphite polymorphs are formed by sheets stacked in ABABAB (hexagonal graphite) (Figure 2.8.a) or, less often, in ABCABC order (rhombohedral graphite), with different amounts of stacking faults. Up to one lithium, per six carbon atoms can be intercalated in graphite, giving the \( \text{LiC}_6 \) composition, thus limiting specific capacity of graphite to 372 mAh/g:
Graphene sheet stacking changes upon lithium insertion into a structure so that honeycombs in neighbouring layers directly face each other. In other words, the stacking sequence converts to AAA. The original interlayer distance increases by about 9% in $LiC_6$ (Figure 2.8.b and 2.8.c). This expansion is fully reversed upon de-intercalation of lithium [4].

Non-graphitic carbons consist of small, on the order of few nanometres, disordered graphene sheets, or stacks of several such sheets [24]. These carbons can also be divided into two classes:

- soft or graphitisable carbons,
- hard or non-graphitisable carbons.

Soft carbons develop graphitic structure upon heat treatment at temperatures over 2000 °C. In hard carbons highly disordered and cross-linked graphene layers are unable to realign and thus hard carbons cannot assume graphitic structure at any temperature.
Dahn et al. [23] also distinguishes hydrogen containing carbons. This type includes both hard and soft carbons heat-treated below approximately 800 °C. Hydrogen containing carbons have high reversible capacities approaching 1000 mAh/g. However, they also exhibit high irreversible capacities during the first cycle, and large voltage hysteresis with lithium intercalation happening just over 0 V and de-intercalation – around 1 V vs. Li/Li⁺. The specific capacity of soft carbons decreases quickly to around 300 mAh/g with the increase of carbonisation temperature to 1000 °C or slightly higher. Conversely, hard carbons exhibit relatively high capacities of around 600 mAh/g when carbonised at temperatures around 1000 °C. Combined with good cycling stability and a relatively small voltage hysteresis this property makes hard carbons a promising anode material.

Several models have been suggested to explain the high specific charge of non-graphitic carbons [25]. Dahn et al. suggested that graphene sheets in hard carbons are arranged in a ‘house of cards’ or ‘falling cards’ manner, and that lithium is adsorbed on both sides of such sheets [23,26,27]. Several researchers proposed that considerable amount of lithium can be stored on edges and surfaces of small graphite particles [28,29]. Sato et al. suggested that lithium molecules occupy nearest neighbouring sites in carbons [30]. Others proposed that lithium can be deposited in multilayers on graphene sheets [31]. It was also suggested by Fujimoto et al. that additional lithium can be stored in nanoscopic cavities between carbon particles [32].

2.3.5.2. Lithium-metal alloys and related materials

The possibility of electrochemical lithium alloying into a number of metals has been demonstrated by Dey as early as 1971 [33]. Figure 2.9 demonstrates that these
materials have specific capacities significantly higher than graphite and other carbons. Considering specific capacities in combination with such parameters as material abundance, cost and toxicity, aluminium, tin and silicon seem to be the most promising candidates to replace carbon anodes [34]. Silicon is far ahead in terms of its gravimetric capacity that is approximately four times higher than capacities of aluminium and tin. A large number of intermetallic compounds, for instance $Cu_6Sn_5$ [35], have also been considered as possible anode materials for lithium batteries.

![Figure 2.9](image)

**Figure 2.9.**

Specific capacities towards lithium of selected metals and semiconductors.

Despite obvious advantages, lithium alloys have so far found only limited application in commercial batteries, mainly due to pulverisation during cycling and consequent loss of electronic contact with the current collector. The volume of graphite increases by approximately 10 % upon lithium intercalation; in contrast, high capacity metals typically experience 2 to 4 fold volume swings during lithium alloying-dealloying, which leads to mechanical disintegration of anode materials during repeated cycling and
loss of electronic contact with the current collector or conductive additives. Several approaches have been used by researchers to overcome the poor cycle life of alternative anode materials, the most promising of them being to decrease particle dimensions, create matrices that prevent pulverisation of active material, introduce porosity in the electrode structure or some combination thereof. Examples of these methods will be discussed in Chapter 3.

2.3.5.3. **Silicon**

Silicon negative electrodes show by far the highest gravimetric and volumetric specific capacities towards lithium of all materials that have been studied as anodes in lithium cells except of metallic lithium itself (see Figure 2.9). High capacity, combined with an attractive voltage profile, silicon abundance, low cost and environmental ‘friendliness’, makes silicon a very promising anode material.

However, silicon still has not been implemented in commercial batteries. The main problems that reduce performance of silicon anodes are:

- low electronic conductivity of silicon,
- slow lithium diffusion,
- huge (up to 400 %) volume changes that material experiences during cycling.

Silicon was first proposed as a negative electrode material for high temperature lithium cells with molten salt electrolytes in mid-1970s [36,37]. In such cells, formation of several different crystalline Li-Si phases has been observed during electrochemical lithium insertion and extraction, the most lithiated phase being $Li_{22}Si_5$ [38], which corresponds to a specific capacity of 4199 mAh/g or 9800 mAh/mL.
Li-Si systems behave quite differently at room temperature. XRD studies of Li-Si alloys at different degrees of lithiation demonstrate that the crystal structure of silicon is destroyed during lithium insertion and an amorphous Li-Si structure is formed [39,40]. At potentials below 50 mV vs. Li/Li⁺ a crystalline compound with the structure Li₁₅Si₄ is formed. Formation of Li₂₂Si₅, the phase expected from the Li-Si phase diagram [41], is not observed at room temperature. The Li₁₅Si₄ (Li₃.₇₅Si) composition corresponds to a theoretical capacity of 3579 mAh/g. During extraction, crystalline Li₁₅Si₄ is converted to amorphous lithiated silicon, which, in turn, converts to amorphous silicon upon complete lithium extraction.

Galvanostatic cycling of both crystalline and amorphous silicon electrodes demonstrates that limiting the lithium insertion voltage to above 50 mV vs. Li/Li⁺ significantly improves cycling performance, because it prevents the formation of the crystalline Li₁₅Si₄ phase. Formation of two phase regions is believed to induce high internal stresses, leading to pulverisation of electrode material and capacity fade. Performance of silicon anodes can also be significantly improved by the use of nanomaterials as discussed in Chapter 3.

2.4. Conclusions

The working principles of battery and particularly lithium-ion battery operation are described in this chapter; requirements that good lithium battery electrolyte, separator and electrode materials should meet are discussed. Additionally, some of the materials widely employed in lithium-ion batteries, as well as promising electrode materials, are reviewed. Properties of carbonaceous and silicon-based negative electrode materials are discussed in some more detail.
2.5. References


CHAPTER 3.

NANOSTRUCTURED ELECTRODE MATERIALS FOR LITHIUM-ION BATTERIES

3.1. Preamble

Nanomaterials are defined as materials that have at least one spatial dimension in the size range of 1 nm to 1 μm [1]. These materials have received broad attention, especially in the last decade, due to their unusual physical and chemical properties. These properties, and the mere fact that they are often size- and shape-dependent, opens new horizons in such diverse scientific and technological areas as optics, electronics, energy storage and conversion, catalysis. Nanostructured materials are attracting increasing attention in the field of lithium-ion batteries [2].

In this chapter I discuss the main benefits of nanostructured lithium battery electrodes, as well as the challenges associated with their use, with special attention being paid to silicon-based materials. A brief review of inverse opals and of composites based on inverse opal structures that have been suggested for use as lithium-ion battery electrodes is also given in this chapter.

3.2. Nanostructured Electrode Materials

3.2.1. General considerations

It is now commonly accepted that nanostructured materials demonstrate improved performance compared to their bulk counterparts when used as electrode materials in
lithium-ion batteries. This can even be illustrated by the example of carbonaceous electrodes: non-graphitic carbons, essentially composed of nanosized graphene sheet stacks, show much higher reversible capacities than the theoretical capacity of graphite. Nanostructured materials also provide new opportunities for the development of batteries with advanced architectures, *e.g.* thin-film and flexible batteries [3]. The major benefits of nanomaterials are:

- dramatically reduced lithium diffusion distances, which translate into high rate capabilities;
- high surface areas, that allow faster lithium absorption and again increased rate performance;
- large surface area to volume ratios might somewhat reduce the mechanical stress associated with volume swings during lithium insertion-extraction, improving the cycling behaviour.

However, high surface areas can also enhance side reactions of electrode materials, such as with the electrolyte, causing high irreversible capacities. The density of nanopowders is usually less than the density of the same bulk material, so the volume of electrodes increases for the same mass of material reducing the volumetric energy density.

Various approaches allowing the utilisation of nanomaterials in lithium-ion battery electrodes have been used, including the following:

1. Use of thin films of active material deposited directly on current collectors. Films of pure materials provide higher specific capacities as they do not contain any binders and conductive additives. However, such electrodes can be practically
employed in miniature and microbatteries only, as these films have to be sufficiently thin in order to ensure high lithium diffusion rates and electronic conductivity. Also, the thinner the film, the better it accommodates volume changes associated with lithium insertion-extraction, while thicker films quickly detach and lose electronic contact with the current collector [4].

2. Methods analogous to that used for preparation of conventional electrodes; *i.e.* nanosized particles are dispersed in a mixture of a binder (usually PVdF, polyvinylidene fluoride) and a conductive additive (carbon black). This method improves rate capabilities and cycling behaviour of many electrode materials [5], but it has a limited effect on materials that exhibit large volume changes during cycling, as the soft polymer-carbon matrix does not possess the mechanical properties necessary to prevent pulverisation [6].

3. Use of nanosized particles, dispersed in an inactive hard matrix. This method allows for better capacity retention in the case of alloy anodes, as the matrix accommodates volume changes in the active material and prevents its pulverisation. An elegant way of *in situ* inactive matrix creation was suggested by Idota *et al* [7]. Electrochemical reaction of lithium ions with tin oxides resulted in the creation of metallic tin and $Li_2O$ inactive matrix, which alleviates the effects of volume changes during reversible lithium alloying with tin (Equation 3.1).

$$SnO_2 + 4Li^+ + 4\overline{e} \rightarrow Sn + 2Li_2O$$

$$Sn + xLi^+ + x\overline{e} \leftrightarrow Li_xSn, \ 0 \leq x \leq 4.4$$  \hspace{1cm} \text{Eq. 3.1.}$$

The inactive matrix significantly reduces the specific capacity of the electrode and, if created *in situ*, causes high irreversible capacity during the first cycle.
4. Use of nanosized particles, dispersed in an electrochemically active matrix. This method is often used for nanostructured high capacity negative electrode materials. Composites of such materials with carbons often demonstrate high rate capability and reasonable cyclability due to high carbon conductivity and its ‘cushion’ effect that reduces material pulverisation and ensures good electronic contact with nanoparticles.

5. Use of porous networks of electroactive materials with nanosized pores and walls. These materials and inverse opal structures in particular are discussed in some detail in Section 3.3.

### 3.2.2. Silicon-based materials

The use of nanostructured materials is particularly promising in the case of silicon-based negative electrodes, as these materials can eliminate or at least greatly reduce problems associated with such properties of silicon and lithium-silicon alloys as low conductivity, slow lithium diffusion and huge volume swings.

The electrochemical behaviour of amorphous and nanocrystalline silicon thin films has been examined in numerous studies. These films are usually prepared by means of various vapour deposition techniques. Generally, thinner films demonstrate better cycling performance than thicker ones; electronic conductivity of silicon is also very important to the electrode performance. The most impressive example of thin film silicon anodes was demonstrated by Takamura et al [8]. A 50 nm thick film of P-doped n-type silicon showed a stable reversible capacity of 3600 mAh/g for 200 cycles at 2C rate, and a reversible capacity over 2000 mAh/g was obtained at a 30C rate, which was stable for 3000 cycles.
Simple reduction of silicon particle size to nanoscale and successive mixing nanoparticles with a binder and a conductive additive already allows significant improvement of electrode performance [9]. However, capacity fading during cycling remains too high to allow implementation of such electrodes in practical lithium-ion cells.

A large number of compounds have been used as inactive matrices supporting silicon nanoparticles. Silicon has been mixed by high-energy mechanical milling with hard conductive ceramics, such as TiN, TiC, TiB$_2$ [10-12]. Such composites demonstrated good cyclability, however, their capacities were low, probably due to poor Li$^+$ diffusivity in the ceramic matrix. Silicon-metal alloys were also prepared by high-energy mechanical milling of silicon with iron or nickel [13]. A metallic matrix forms during initial lithium insertion, allowing reversible silicon-lithium alloying during further cycling:

$$MSi + xLi^+ + x\bar{e} \rightarrow M + Li_xSi$$

$$M + Li_xSi \leftrightarrow M + Si + xLi^+ + x\bar{e}$$

Eq. 3.2.

Such composites demonstrated high initial capacities that faded quickly during cycling. Lithium oxide inert matrices were created from silicon oxides with different oxygen contents $SiO_x \ (0.8 \leq x \leq 1.1)$ [14]. The mechanism of $LiO_2$ formation is analogous to the tin oxide case [7]:

$$SiO_x + 2xLi^+ + 2x\bar{e} \rightarrow Si + xLi_2O$$

$$Si + yLi^+ + y\bar{e} \leftrightarrow Li_ySi$$

Eq. 3.3.
These materials showed high specific capacity and good cycle life, but high irreversible capacity due to $Li_2O$ formation on the first cycle makes them less attractive for practical applications.

Use of an active matrix that itself reversibly inserts and extracts lithium, increases capacity and in many cases capacity retention of a silicon-based electrode. Electrode performance of silicon composites and alloys with electroactive metals, such as magnesium [15], silver [16] and tin [17] have been studied. These materials demonstrate poor capacity retention mainly due to high volume swings of both composite components during lithium insertion-extraction and to multiple phase transitions as in the $Mg-Si$ system. Carbon has been used as an active matrix for nano-silicon anodes in numerous studies and proved to be the most apt choice so far. Several approaches have been used for synthesis of silicon-carbon composites:

- Mechanical milling allows preparation of composites with desired structure, silicon to carbon ratio and particle sizes [18]. However, high-energy mechanical milling significantly reduces the amount of electroactive material due to the formation of silicon carbide $SiC$ [19]. Besides that, such materials often demonstrate significant capacity fading because of macrostructural electrode deformations caused by microstructural changes during lithium insertion-extraction [6,20].

- Silicon nanoparticles can be deposited on larger carbon particles by chemical vapour deposition (CVD) from silanes or chlorosilanes (see Section 6.2.1 for the details of silicon CVD) [21-23]. This strategy allowed Holzapfel et al. [23] to produce graphite-silicon composites that demonstrated reversible capacity of
about 1000 mAh/g and reasonable cycling behaviour with the capacity loss of less than 1 % per cycle. However, the initial irreversible capacity of such materials is still an issue.

- Silicon-carbon composites can be prepared by dispersing silicon nanoparticles in a gel carbon precursor (see Section 7.2.2 for some examples of such precursors). Wang et al. [24] synthesised a composite material containing homogeneously distributed nanosized silicon particles in a carbon matrix pyrolysed from resorcinol-formaldehyde based aerogel. This material demonstrated reversible capacity close to 1500 mAh/g and excellent capacity retention for 50 cycles.

### 3.3. Macroporous Electrode Materials

#### 3.3.1. Introduction

Macroporous nanostructured materials fabricated in the form of inverse opals provide several advantages when used as lithium-ion battery electrodes:

- Distances of lithium solid-state diffusion are kept short since the wall thicknesses are on the order of nanometres to tens of nanometres, which improves rate capabilities of the electrodes;
- Relatively large surface area decreases the current density, again increasing rate performance;
- Macropores with the size range of several hundred nanometres enable easy infiltration of electrolyte and fast liquid-phase lithium diffusion, reducing the concentration polarisation and increasing rate performance and capacity of the cell;
• Continuous network of electrode material may provide better electrical conductivity than aggregates of loosely connected particles;
• Macroporosity should help to accommodate volume swings during cycling without losing structural integrity of the electrode.

This type of electrode necessarily has reduced energy density comparing to bulk materials due to its high porosity. Despite this limitation, macroporous structures seem to be a very promising material architecture for battery electrode materials.

Electrochemical behaviour of inverse opal lithium-ion battery electrode materials has been studied by several research groups in recent years. The first report on such a material was published in 2001 [25]. Take et al. used carbon inverse opal as an anode, however only very limited electrochemical data was provided at the time. In 2002 Sakamoto and Dunn reported the synthesis and electrochemical behaviour of vanadia gel inverse opal cathode [26]. The study demonstrated excellent behaviour of ordered macroporous structures at high current rates. Since then several more electroactive materials have been synthesised in the inverse opal form and tried as both positive and negative electrodes.

3.3.2. Cathode materials

Sakamoto and Dunn [26] synthesised \( V_2O_5 \) ambigel inverse opal by infiltrating a polystyrene colloidal crystal with the solution of vanadyl triisopropoxide oxide, room temperature hydrolysis and condensation of vanadia gel in water vapour and subsequent removal of the polystyrene template with cyclohexane. Thusly prepared electrodes could be reversibly cycled and demonstrated impressive rate capabilities, with the capacity reduced by a factor of 2.5 when discharge rate was increased by a factor of 100.
Lu et al. [27] obtained well-crystallised $\text{LiFePO}_4$ inverse opals by calcining under nitrogen the precursors of $\text{Li}^+, \text{Fe}^{2+}$ and $\text{PO}_4^{3-}$ in the presence of a latex colloidal crystal template. Again, good behaviour at high current rates was demonstrated. The material exhibited capacities close to theoretical values at low current rates (C/10 to 1C), and still retained about 60% of its low rate capacity when cycled at the rate of 5.9C.

$\text{LiCoO}_2$ inverse opals were synthesised by infiltrating opal made of poly(methyl methacrylate) microspheres with a mixture of lithium acetate and cobalt acetate, drying, and calcining at 500-800 °C [28]. Although at low current rates cyclability of macroporous electrodes was inferior to bulk material, at C/2 and higher current rates only inverse opal structures were able to maintain reasonable capacity.

### 3.3.3. Anode materials

After the initial brief report by Take et al. [25] electrochemical properties of carbon inverse opal anodes were investigated by two research groups [29-31]. Stein and colleagues [29,30] synthesised hard carbon inverse opal by polymerisation of resorcinol-formaldehyde precursor, while Su et al. [31] prepared graphitic inverse opal by chemical vapour deposition from benzene. Both materials demonstrated specific capacities from 200–370 mAh/g, good cyclability and good high rate performance.

Several research groups investigated the electrochemical behaviour of anatase $\text{TiO}_2$ inverse opal electrodes for lithium-ion batteries [32-36]. In most cases anatase has been prepared via a sol-gel process from titanium tetraisopropoxide solutions. Electrodes demonstrated mediocre cyclability at best, but their capacities at high rates were usually better than capacities of bulk materials. It was also noted that rate capability increases with decreasing pore size [32,33].
\(Li_4Ti_5O_{12}\) inverse opals prepared by sol-gel method have been also used as lithium-ion battery anode material [37-39]. Unlike anatase electrodes, \(Li_4Ti_5O_{12}\), synthesised by Sorensen et al. [39], demonstrated a capacity close to the theoretical value, high cycling stability and exceptional rate capability.

Stein and colleagues synthesised cassiterite \(SnO_2\) inverse opals by sol-gel method and studied their performance as anode for lithium-ion batteries [40]. The material experienced less polarisation than tin oxide electrodes with other geometries during the first lithium insertion, indicating that inverse opal architecture is beneficial for high rate applications. However, capacity dropped sharply after the first cycle. SEM images revealed immense irreversible swelling of the material decreasing the pore size, or even completely blocked the pores.

Recently a series of intermetallic tin alloy inverse opals have been employed as lithium-ion battery anodes [41-43]. \(Sn-Ni\), \(Sn-Co\) or \(Sn-Cu\) alloys were electrodeposited into the voids of polystyrene colloidal crystal films. All materials demonstrated high capacities of 400–700 mAh/g and reasonable cyclability (capacity retention of 93.7 % after 75 galvanostatic cycles in the case of tin-cobalt alloy [42]). Cycling stability was found to improve with decreasing template sphere size [43].

### 3.3.4. Composites based on inverse opal architectures

Composite materials based on inverse opal structures have been suggested to be used as lithium-ion battery electrodes [29-31,44], as solid electrolyte – electrode combinations [45,46], and even as complete three-dimensional interpenetrating solid-state lithium-ion cells [47,48].
Carbon inverse opals have been employed as a basis for most composite electrodes (both positive and negative), as they can serve as a light matrix with high electronic conductivity and good structural stability that is maintained during cycling. Deposition of active electrode materials onto the carbon inverse opals allows for the combination of the benefits of thin film electrodes (short lithium diffusion lengths and electron paths, better accommodation of structural changes during lithium insertion-extraction) with the advantages of macroporous electrodes. However, this becomes possible only at the expense of specific capacity that is somewhat lowered by the carbon matrix, especially in the case of positive electrodes.

A brief review of the literature devoted to composites based on inverse opal structures is given in Section 8.2.

3.4. Conclusions

Properties of nanostructured lithium-ion battery electrodes were discussed in this chapter, with the main advantages of such materials and problems associated with them being highlighted. Potential benefits and disadvantages of the use of inverse opals – a particular type of nanostructured electrodes – are discussed in some more detail, and the literature devoted to inverse opal electrodes is briefly reviewed.

3.5. References


CHAPTER 4.
MATERIAL CHARACTERISATION METHODS

4.1. Preamble

Adequate material characterisation is an important part of creating materials with desired properties. Choosing appropriate techniques for the characterisation of thin film materials having composite structure and complex morphology is a non-trivial task. The materials synthesised and studied in this work were characterised by a variety of analytical techniques that provided valuable information on their structure, morphology, elemental composition, physical and chemical properties.

Methods used for the characterisation of the as-synthesised electrode materials and materials after electrochemical cycling, such as optical and electron microscopy, spectroscopy, x-ray scattering techniques, thermogravimetric analysis and electrical conductivity measurements, are described in Section 4.2. Section 4.3 deals with the methods used to evaluate electrochemical performance of the materials, namely with cyclic voltammetry and galvanostatic cycling.

4.2. Physical and physico-chemical characterisation methods

4.2.1. Optical microscopy

Although simple, optical microscopy is an important technique for the study of colloidal crystal films due to the fact that the lattice parameters of such crystals are on the same order of magnitude as the wavelength of visible light. This allows for the easy identification of structural defects and a quick assessment of the quality of the film.
Optical microscopy applied to the study of colloidal crystals can be compared to high-resolution transmission electron microscopy (HRTEM) used for characterisation of atomic crystals.

All optical microscopy images presented in this thesis were taken using an Olympus BX41 research microscope combined with a PixeLINK PL-A642 megapixel firewire digital camera. This system allows for the resolution of about 300-400 nm.

4.2.2. Scanning electron microscopy

Arguably, the most valuable characterisation tool available to materials scientists is scanning electron microscopy (SEM), as it allows for the direct visualisation of materials with resolutions far beyond the capabilities of optical microscopy. SEM is based on imaging using a tightly focused electron beam, which scans the surface of the sample. Interactions of the beam with matter produce a variety of detectable species, such as secondary and Auger electrons, X-rays, etc. Secondary electrons are the primary source for material visualisation by SEM, as only electrons originated in the area directly under the beam within a few nanometres from the sample surface can escape from the material due to their low energy, and thus be detected [1].

The SEM images presented in this thesis were obtained using one of two field emission scanning electron microscopes: the Hitachi S-4500 and Hitachi S-5200. The resolution of the former microscope is on the order of 5 to 10 nm, while the resolution of the latter achieves values as low as 0.4 nm.

Several precautions have to be taken to transfer materials after electrochemical cycling into the SEM without exposing them to ambient atmosphere. Firstly, the coin cells were disassembled in an M. Braun Inertgas-Systeme GmbH UNILab glove box
filled with argon with oxygen and water content kept below 1 ppm, electrode material was thoroughly washed with dimethyl carbonate, dried and put onto an SEM sample holder, which was then tightly sealed in a gas-proof container. Secondly, this container was transferred into an argon-filled two-sleeve glove bag directly attached to the SEM inlet port, the container was opened and the SEM sample holder was loaded into the microscope.

4.2.3. **Energy dispersive X-ray spectroscopy**

Energy dispersive X-ray spectroscopy (EDX) is a technique used for a non-destructive elemental analysis of solid materials. It relies on detection of characteristic X-rays emitted when electrons ‘hop’ from higher energy outer shells to inner shells. The sample needs to be irradiated with a high energy beam in order to eject electrons from their shells and induce X-ray emission [2].

The Hitachi S-5200 SEM is equipped with the INCAx-sight EDX spectrometer from Oxford Instruments, which allows performing elemental micro-analysis and element mapping of the samples imaged by SEM.

It should be noted that quantitative results obtained by EDX spectroscopy are to be taken with caution when samples with complex morphology on the micro-scale have been analysed. On the one hand, knowledge of the exact position of the detector (both in distance and angular terms) from the sample surface is vital for accurate quantitative analysis of the data collected. On the other hand, although the maximum distance inside the material at which X-rays are generated depends on the energy of irradiating electrons, material composition and density, it is usually comparable to the thickness of inverse opal
walls. This makes the angle at which the detector is located in relation to the sample surface unpredictable and, hence, diminishes the reliability of the results.

4.2.4. **X-ray photoelectron spectroscopy**

X-ray photoelectron spectroscopy (XPS) is a quantitative technique that provides information on the elemental composition and chemical state of the elements within several nanometres from the material’s surface. XPS is based on irradiating sample with an X-ray beam and simultaneously measuring the number and energy of electrons photoemitted from the material close to its surface [3].

The XPS spectra presented in this thesis were collected using the Thermo Fisher K-Alpha X-ray photoelectron spectrometer with a monochromatic $Al\ K_\alpha$ X-ray source. This system allows collecting data on a spot as small as 30 μm.

4.2.5. **Raman micro-spectroscopy**

Raman spectroscopy is used for studying vibrational, rotational, and other low-frequency modes in condensed matter. It is based on the inelastic Raman scattering of monochromatic light, usually from a laser. Confocal Raman microspectroscopy is a powerful technique for material microanalysis as it allows collection of data from very small volumes of the material. Depending on the laser wavelength and system characteristics lateral resolutions of about 1 μm can be achieved [4].

The Raman spectroscopy of the materials described in this thesis was performed using a modified JY LabRam confocal microraman spectrometer with a green doubled Nd:YAG laser (532 nm) and 1024×256, 16 bit CCD detector. The laser power was kept at 10-20 kW/cm$^2$ to avoid sample overheating. The spectra were collected from areas with diameters of 10 to 50 μm.
The materials after electrochemical cycling used for Raman spectroscopy had to be protected from atmosphere. After a coin cell was disassembled in the M. Braun argon-filled glove box, washing and drying the film, it was sandwiched between two glass cover slips. The cover slips were sealed together with a 75 μm thick Surlyn sealant resin from DuPont by careful heating with a handy sealer (Figure 4.1).

![Figure 4.1.](image)

Scheme of sample sealing used for μ-Raman of cycled materials: 1,4 cover slips; 2 sample; 3 Surlyn sealant resin.

4.2.6. **Powder X-ray diffraction**

Powder X-ray diffraction (PXRD or XRD) is an analytical technique that provides structural characterisation of powdered or microcrystalline materials. It is based on the elastic scattering of X-rays from the materials that possess long range order. XRD data provides information on the crystallographic structure and crystallite size of materials [5].

XRD patterns were collected using the Siemens/Bruker AXS D5000 diffractometer equipped with high power line-focus Cu X-ray source. For a typical analysis several inverse opal films were finely grinded together, placed on a low background quartz slide and scanned in the desired range of scattering angles 2Θ.
4.2.7. Thermogravimetric analysis

Thermogravimetric analysis or TGA is a method of analysis performed to determine changes in weight of the sample in relation to change in temperature. SDT Q600 analyser from TA Instruments was used for the TGA analyses presented in the thesis. Typically, five to ten inverse opal films were finely grinded, placed in an alumina pan and then heated at a slow rate of 2 °C/min to 700-1400 °C under a constant air flow. This procedure ensured complete oxidation of the material and allowed estimation of its elemental composition.

4.2.8. Conductivity measurements

DC electrical conductivity of inverse opal films was determined by two-probe method using the Keithley 6517 electrometer / high resistance meter. Inverse opal films used for conductivity measurements were synthesised on high resistive substrates, such as Corning EAGLE glass, quartz or sapphire. Two square 1 cm co-planar aluminium electrodes, separated by 1 mm were deposited onto the sample film via physical vapour deposition. A certain bias voltage was then applied for ten minutes, after which current was recorded, the bias voltage was changed and held for 5 minutes before recording the next measurement. Usually 8 to 10 measurements at different positive and negative voltages were performed. Resistance \( R \) was then found from the slope of current–voltage linear curve, and the conductivity \( \sigma \) was calculated by Equation 4.1:

\[
\sigma = \frac{l}{Rah}
\]

Eq. 4.1,

where \( l \) is the distance between electrodes (0.1 cm), \( a \) is the width of electrode (1 cm) and \( h \) is the film thickness determined by cross-sectional SEM.
4.3. Electrochemical Characterisation Techniques

Electrochemical properties and performance of battery electrodes can be characterised by a variety of techniques. Cycling voltammetry (CV) and galvanostatic cycling are the two most widely used and probably most informative DC methods for electrode behaviour characterisation.

4.3.1. Electrochemical Cell Preparation

All electrochemical testing of electrode materials under study was performed using standard coin cells type 2325 from NRC Canada with lithium metal as a counter electrode. The scheme of the coin cell is outlined in Figure 4.2. The body of the cell consists of stainless steel current collectors 1 and 9 separated by a polypropylene gasket 8. The inverse opal films 2 are put directly on the current collector 1, followed by Celgard 2340 polypropylene-polyethylene-polypropylene microporous separator 3. Liquid electrolyte 4 composed of 1 M LiPF$_6$ in 1:1 ethylene carbonate – dimethyl carbonate mixture is then infiltrated into the separator and inverse opal electrode. After the addition of electrolyte lithium metal foil 5, stainless steel spacer 6 and belleville style stainless steel spring 7 are put on top of the separator. The cell is then completed with gasket 8 and current collector 9 and sealed by a specially designed pneumatic coin cell crimper from NRC Canada. The cell assembly was always performed in argon-filled glove box from M. Braun Inertgas-Systeme GmbH, where contents of water and oxygen were maintained at levels below 1 ppm. After assembly cells were allowed to rest for at least one hour before electrochemical testing to ensure proper infiltration of electrolyte into the pores of the separator and macroporous electrode material.
4.3.2. Cyclic voltammetry

Cyclic voltammetry is a simple, useful electroanalytical tool with which to understand the fundamental electrochemical behaviour of electrode materials for lithium-ion batteries. CV is a potentiodynamic technique, during which the voltage is ramped linearly vs. time. When a certain set voltage $E_1$ or $E_2$ is reached the ramp direction is inverted as shown in Figure 4.3. Ramping can be performed at different scan rates measured in V/s. The data obtained in the CV experiment is then plotted as specific current $i$ expressed in mA/g vs. potential $E$ (V) [6]. All cyclic voltammetry experiments were performed using the Solartron 1287 potentiostat and the data was collected with the Corrware 2.6b software.
4.3.3. **Galvanostatic cycling**

Galvanostatic cycling is the main tool used for characterisation of electrode lithium storage capacity and cycling behaviour. In galvanostatic experiment a certain current is applied to the cell or produced by the cell. When a high or low voltage limit is reached the current direction is reversed as demonstrated in Figure 4.4. Specific capacities of an electrode $C_{in}$ and $C_{out}$ for lithium insertion and extraction can be obtained and coulombic efficiency $C_{out}/C_{in}$ can be calculated for each cycle from galvanostatic cycling experiments. Galvanostatic cycling can also be performed at different current rates allowing evaluation of material rate capabilities. Galvanostatic testing of the materials under study was performed using either the Solartron 1287 potentiostat or MacPile II multichannel potentiostat from Bio-Logic SAS.
4.4. References


5.1. Preamble

Materials intended for use as sacrificial templates for syntheses of macroporous Li-ion battery electrodes should meet certain requirements, which are in turn dictated by synthetic, manufacturing and economic conditions. Namely, the material should be cheap and simple to produce, as well as stable chemically, thermally and mechanically, so that they can withstand harsh conditions such as silicon CVD or polymer carbonisation. At the same time the material of choice should be easily removed following templating.

Considering these requirements, artificial silica opals seem to be a nearly ideal candidate for template material. The synthesis of silica spheres is relatively simple and can be scaled up. Colloidal crystals can be easily assembled into large colloidal crystals, especially if high optical quality is not a requirement, which it is the case for an electrode material. Silica particles are inert to most chemical reagents, and silica opals retain their porous structure when heated to at least 600 °C or higher, if a material is to be infiltrated in the inter-sphere pores at such high temperatures. Silica can be easily and selectively dissolved by dilute fluoride solutions or by strong bases if the use of fluoride is undesirable.

In this chapter I present details on the synthesis of monodisperse silica microspheres, different techniques used to fabricate silica colloidal crystals and a method to enhance their mechanical strength.
5.2. Synthesis of Monodisperse Silica Microspheres

Silica microspheres are most often synthesised by a sol-gel process which involves hydrolysis of silicon alkoxides and subsequent polycondensation to form Si-O-Si bonds. This synthetic method was first proposed in 1968 by Stöber and colleagues [1], and hence is generally referred to as the Stöber method. The overall reaction for this process is:

\[
Si(OR)_4 + 2H_2O \rightarrow SiO_2 + 4ROH \tag{Eq. 5.1}
\]

The nucleation and growth mechanism for the formation of silica microspheres from silicon alkoxides (particularly from tetraethyl orthosilicate, TEOS) is well understood [2]. The process starts with the formation of small silicate oligomers, which then condense into larger nuclei or seeds that continue to grow by accretion of silicate oligomers. The growing silica particles acquire a spherical shape in order to minimise their surface free energy. These microspheres then maintain their growth either until silicate precursors are depleted in the solution or the repulsion from the negatively charged surface of the silica microspheres becomes too high to allow for the deposition of additional silicate. The resulting silica spheres are relatively monodisperse, with diameters of up to 550 nm, depending on the reaction conditions. The microspheres synthesised by the Stöber method consist of amorphous, microporous silica with the refractive indices ranging from 1.40 to 1.43 [3], which is slightly lower than the refractive index of dense silica \((n = 1.455-1.470 \text{ in the visible spectral range}) [4]\.

Monodisperse silica spheres of three different diameters were used in this study: Ø 250 nm, Ø 480 nm and Ø 890 nm. Spheres were synthesised by a modified Stöber method, which involved multiple re-growth cycles as described by Giesche [5]. In brief,
hydrolysis of tetraethyl orthosilicate and polycondensation of silica is performed in anhydrous ethanol medium in the presence of ammonium hydroxide as a catalyst. The reagents are added drop-wise into a heated flask under an atmosphere of nitrogen, as shown in Figure 5.1. The Giesche modification of the original Stöber method is based on the use of smaller spheres as “seeds” for subsequent re-growth to larger diameters in several steps. This allows a better control over the growth conditions and provides improved monodispersity. The seeds usually have a polydispersity of about 5-10 %, so the diameters of 200 nm seeds differ by up to 20 nm. This absolute variation is more or less held during re-growth, so that the final 800 nm spheres would also possess the diameter variation of 20 nm or less. This allows the production of spheres with a final dispersity of about 2.5 %.
Figure 5.1.

Set-up for the synthesis of colloidal silica microspheres by the Stöber method: solutions of TEOS/ethanol and ammonia/water/ethanol are introduced drop-wise into the reaction flask.

After synthesis the spheres were meticulously cleaned by centrifuging, decanting, and re-dispersing in de-ionised water for three times and then in ethanol until no ammonia odour could be observed.

A small amount of doublets and triplets (two or three spheres fused together) and spheres of smaller diameter (secondary seeds) are always present in the final dispersion of silica microspheres prepared by this method. Removal of the multiplets and the secondary seeds is achieved by sedimentation fractionation in a column.

It was demonstrated by Chabanov et al. [6] that pre-sintering of the silica spheres reduces their subsequent shrinkage during high temperature processing of colloidal crystals, and hence allows one to minimise cracking of the colloidal crystal templates. So the last step of the silica microspheres synthesis involved heating pre-cleaned spheres in
air at 450 °C (spheres with the diameter of 250 nm) or at 600 °C (480 nm and 890 nm spheres) for 8 hours. Spheres were then re-dispersed and cleaned in water and ethanol as described earlier in this section.

5.3. Growth of Colloidal Crystal Film from Monodisperse Silica Spheres

Crystallisation of the silica microspheres into three dimensionally ordered arrays – colloidal crystals or artificial opals– is central to syntheses of materials described in the following chapters. Most of the techniques employed for colloidal crystal preparation can be broadly divided into two categories: methods based on sedimentation [7-11] and evaporation induced self-assembly [12,13] as well as its modifications.

These methods produce close packed arrays of microspheres, that are usually considered to have a face centre cubic (fcc) crystal structure. However, stacking faults readily occur during growth [14] creating deviations in the stacking of the {111} planes parallel to the substrate from a periodic ABCABC... sequence to a random one, as there is only a minute difference in the energy of formation of fcc and hexagonal close-packed (hcp, ABABAB…) lattices of hard spheres [15]. The resulting structure, called random hexagonally close-packed (rhcp), can be regarded as a mixture of fcc and hcp lattices.

5.3.1. Sedimentation

Colloidal sedimentation methods utilise the fact that the settling of particles in the gravitational field is slowed down by the viscous medium. If silica particles in the suspension descend slowly enough they self-assemble into a close-packed colloidal crystal at the bottom of a sedimentation column. The terminal velocity of a particle
falling in the viscous fluid under its own weight is reached when the combination of the frictional force and the buoyancy force exactly balances the gravitational force. The resulting velocity of spherical particles in a dispersion can be calculated by combining the equation for buoyant force, the Stokes’ law and the gravitational law:

$$V_s = \frac{2}{9} \frac{r^2 g (\rho_p - \rho_f)}{\mu}$$  \hspace{1cm} \text{Eq. 5.2,}$$

where $V_s$ is the particles' settling velocity, $r$ is the radius of the particle, $g$ is the gravitational acceleration, $\rho_p$ and $\rho_f$ are the densities of the particle and of the fluid respectively, and $\mu$ is the dynamic fluid viscosity.

For sphere diameters in excess of 550 nm, the sedimentation velocity is too high, and an amorphous structure rather then a regular array forms at the bottom of the column. In such case a solvent of higher viscosity, \textit{i.e.} water-glycol mixture can be used to slow down sedimentation; alternatively, an electrostatic field working in the direction opposite to gravitational force can be applied in order to decrease the velocity of charged silica particles [11].

The sedimentation method is indispensable for preparation of large, thick (on the order of millimetre) colloidal crystals. However, the optical properties of materials prepared by this method are usually inferior to crystals made by evaporation induced self-assembly although for making a battery electrode this is not so important.

\subsection*{5.3.2. Evaporation induced self-assembly}

Evaporation induced self-assembly, often referred to as the \textit{Colvin method} as it was first used for growing multilayer colloidal crystal films by the Colvin group [12], is based on sphere self-assembly on a flat vertical substrate in the proximity of solvent-air
interface during solvent evaporation. The evaporation creates a convective flux in the solvent, which transports suspended microspheres to the meniscus. At the contact line between the meniscus and the substrate, the particles form a close-packed array on the substrate, which grows epitaxially as the meniscus moves down with continuing evaporation. After the completion of evaporation a close-packed colloidal crystal film of high quality remains on the substrate. Films can be deposited onto different substrates. The principle of the EISA method is demonstrated in Figure 5.2.
$$k = \frac{\beta L \varphi}{0.605d(1-\varphi)}$$ \hspace{1cm} \text{Eq. 5.3,}

where $d$ is the diameter of the spheres, $\beta$ is the ratio between the velocity of a particle in solution and the fluid velocity and is assumed to be 1, $L$ is the meniscus height, and $\varphi$ is the particle volume fraction. Experimental data gives values of around 300 $\mu$m for $L$ in case of soda-lime glass substrates in ethanolic solutions.

Unfortunately, the Colvin method is not usable for silica spheres with diameters exceeding 450-500 nm, as their sedimentation velocity is higher than the solvent evaporation rate. This leads to gradual depletion of spheres from the meniscus area and results in decrease of the colloidal crystal thickness and eventually prevention of colloidal crystal formation. This limitation can be overcome by increasing the solvent evaporation rate \textit{via} colloidal crystal deposition either at elevated temperatures or at reduced pressures.

One of the modifications of the Colvin method that can be used to grow colloidal crystals of larger silica spheres is the technique called low-pressure evaporation induced self-assembly. Vials of ethanolic silica sphere dispersion and a vertically positioned substrate are kept in a low-pressure chamber during the colloidal crystal film deposition to accelerate the evaporation of the solvent, so that its rate is the same or slightly higher than the sphere sedimentation rate. Depending on the sphere diameter, pressures in the range of 55 to 100 Torr are usually favoured. Pressures lower than 50 Torr cause vigorous solvent boiling, which greatly reduces the quality of colloidal crystal films grown. This technique allows for the fast production of high quality silica and polymer sphere colloidal crystals, as well as binary colloidal photonic crystals [16].
The isothermal heating evaporation induced self-assembly method (IHEISA) [17,18] is another variation of the EISA method. It uses well controlled heating of the solvent to keep the spheres well dispersed during the deposition. In particular, vials containing the sphere dispersions in ethanol are immersed in an ethylene glycol bath heated to 79.8 ± 0.3 °C, very close to the ethanol boiling point. This causes a considerable increase of the solvent evaporation rate (decreasing total deposition time to less than an hour) and also greatly facilitates convective flows.

I used the classical EISA method for deposition of colloidal crystal films from silica spheres with the diameter of 250 nm and sometimes from 480 nm spheres as well. Most of the colloidal crystal films made of 480 nm spheres and all films made of 890 nm spheres used in this work were deposited either by using the low pressure or high temperature modifications of the Colvin method. The EISA-based techniques provide great versatility to the synthesis of silica colloidal crystal films. These methods allow for the deposition of films of any thickness from a monolayer to 40-50 layers of spheres with different diameters on a large variety of substrates (Figure 5.3). Although most of the films used for further processing, as described in the following chapters, were grown on soda lime glass (microscope slides and cover slips) or on silicon wafers, I have also successfully used quartz, sapphire, mica, aluminium, gold and platinum substrates.
5.4. Mechanical Stabilisation of Colloidal Crystals Using Silica Layer-by-Layer Deposition

A certain enhancement of the mechanical strength of silica colloidal crystal films is highly desirable in order to simplify handling of the material and to reduce its cracking and exfoliation from the substrate caused by high temperature treatments during further processing. Mechanical stabilisation can be achieved by interconnecting the spheres, as well as connecting the initial layer of spheres to the substrate with a thin layer of amorphous silica [19]. During this process small ‘necks’ are formed at the sphere connection points, and hence the procedure is sometimes referred to as ‘necking’.

Atomic layer deposition (ALD) is a chemical process at the gas-solid interface used to create extremely thin coatings. The majority of ALD reactions use two volatile chemicals. These precursors react with a surface one-layer-at-a-time in a sequential manner. By exposing the precursors to the growth surface repeatedly, a thin film is deposited.

In brief, a colloidal crystal film on a substrate is subsequently exposed to vapours of water and silicon tetrachloride $SiCl_4$. Water and $SiCl_4$ are placed in two parallel
connected bubblers through which dry nitrogen can be flowed. This flow transports either of the reactants to the reactor chamber where the colloidal crystal is located. A special glass wool filter placed before the reactor ensures the homogeneous laminar flow of the reactive gas in the sample compartment. Exposure of the sample to water vapour leads to coverage of all the spheres in the lattice with a layer of water hydrogen-bonded to the hydroxylated surface of the silica particles. During the next step water chemisorbed on the sphere surface reacts with $SiCl_4$ vapours forming silicic acid $Si(OH)_4$ and $HCl$. The latter helps to catalyse the poly-condensation of $\equiv Si-OH$ bonds to form water and siloxane bonds [20]. This eventually gives rise to the formation of a continuous silica layer that coats microspheres and connects them to each other and to the substrate. A brief scheme of the process is illustrated in Figure 5.4. The procedure in principle can be repeated until full infiltration of the interstices between spheres, so that no macroporosity will be observed (Figure 5.6.b).
Figure 5.4.
Setup for the atmospheric pressure room temperature layer-by-layer growth of silica film from silicon tetrachloride and water vapours onto a colloidal crystal.

5.5. Characterisation Methods

5.5.1. Optical microscopy

Optical microscopy was used to determine the number layers and hence the opal thickness (Figure 5.5.a). It also proved to be an indispensable technique for quick assessment of the quality of opal films (Figure 5.5.b).
5.5.2. **Scanning electron microscopy**

SEM was used to measure the size of the spheres synthesised, as well as to evaluate their polydispersity. In the case of characterisation of the colloidal crystals films SEM imaging allows for a direct estimation of the amount of structural defects and hence the quality of the film, to find the number of layers and film thickness, and to measure lattice parameters (Figure 5.6).
Figure 5.6

SEM images of silica opals: (a) top surface of a pristine silica opal; (b) composite with the pores completely blocked by layer-by-layer deposited silica; (c) cross-sectional view of 100 μm thick opal prepared by sedimentation; (d)-(f) cross-sectional views of opals of various thicknesses deposited by EISA.
5.6. Conclusions

Monodisperse silica microspheres of several sizes were synthesised by sol-gel poly-condensation from tetraethyl orthosilicate. The method used involves re-growth of larger spheres from small seeds to optimise monodispersity (Stöber-Giesche method). Silica colloidal crystals of high quality were prepared from these spheres by evaporation induced self-assembly method or in some cases by sedimentation.

The sizes and size distributions of microspheres were analysed by SEM. The thickness and structure of silica opals were characterised by means of optical microscopy and SEM.

5.7. References


CHAPTER 6.
SYNTHESIS AND ELECTROCHEMICAL CHARACTERISATION OF SILICON INVERSE OPAL FILMS

6.1. Preamble

The synthesis of silicon inverse colloidal crystal was first reported in 2000 [1]. It became the first silicon 3D photonic crystal with a complete photonic band gap at 1.5 μm (a standard wavelength of light used in telecommunications industry) that was synthesised by a bottom-up assembly approach. This was one of the most important practical steps in the formation and development in the field of 3D photonic crystals. The original inverse silicon opal was synthesised from a silica colloidal crystal template made by sedimentation. Static hot-wall chemical vapour deposition was then implemented to infiltrate silicon into the interstices of silica opal. Since then the synthetic procedures were significantly modified and improved [2].

In Section 6.2 I present details of the methods used in this study for fabrication of silicon inverse opals and for their characterisation. The general synthetic procedure is depicted in Figure 6.1. To expand, it consists of the following steps: infiltration of silica opal with silicon by means of chemical vapour deposition (see Section 6.2.1 for details), removal of silicon overlayer by reactive ion etching (Section 6.2.2), opal inversion by $HF$ etching of silica spheres (Section 6.2.3), and conversion of amorphous silicon inverse opals to the nanocrystalline form by high temperature annealing (Section 6.2.5). Silicon
inverse opals were then characterised (Sections 6.2.4 and 6.2.6) by SEM, micro-Raman
(μ-Raman) spectroscopy, X-ray photoelectron spectroscopy (XPS), thermogravimetric
analysis (TGA), X-ray diffraction (XRD) and two probe conductivity measurements.

![Figure 6.1.](image)

General procedure for silicon inverse opal fabrication includes the following steps: infiltration of silica opal
with silicon by means of CVD (1), silicon overlayer removal by RIE (2), silica template removal with HF
etching (3).

The results of electrochemical cycling of silicon inverse opal film electrodes are
presented in Section 6.3. Electrochemical performance of silicon inverse opals was
studied by cyclic voltammetry and galvanostatic cycling at a variety of current rates. The
voltammetric results from the amorphous material are discussed in Section 6.3.1.1 and its
performance under galvanostatic conditions in Section 6.3.1.2. The behaviour of
nanocrystalline electrodes under CV and galvanostatic cycling is covered in
Sections 6.3.2.1 and 6.3.2.2 respectively. Cycled electrode materials were characterised
by means of SEM and μ-Raman spectroscopy (Sections 6.3.1.3 and 6.3.2.3).
6.2. Synthesis and Characterisation of Silicon Inverse Opals

6.2.1. Silicon chemical vapour deposition

6.2.1.1. Introduction

Chemical vapour deposition (CVD) is a reaction at the gaseous/solid interface, which produces a solid film on a substrate surface. CVD allows for the production of coatings made of most metals and metalloids, some non-metallic elements, such as carbon allotropes, and a large number of compounds, including alloys, oxides, nitrides and carbides. It is a very versatile constantly expanding and improving technology widely used for manufacturing of film coatings, powders and monolithic solids. CVD is indispensable in the electronics industry as an essential step in semiconductor and other electronic components production; it is also widely employed in the metallurgical-coating industry for production of coatings on tools, bearings, and other wear-resistant parts [3].

Chemical vapour deposition belongs to the class of vapour transfer processes. Simply, it is a layer-by-layer synthetic process in which the vapour phase chemical constituents react on the surface or in the near proximity of the surface of a substrate to form a conformal solid deposit. Gaseous molecules can be transferred to the deposition site by way of a thermal gradient, pressure gradient, electrostatic acceleration in plasma, or a combination of these driving forces [4]. CVD has important advantages which make it the preferred method for deposition of many materials, including semiconductors. The most important of these advantages can be summarised as follows:

- CVD based on thermal decomposition is not restricted to a line-of-sight deposition which is a general characteristic of physical vapour deposition
methods. Difficult three-dimensional configurations can usually be coated with relative ease.

- The deposition rate is usually high, but it can be easily reduced if necessary by changing deposition parameters.
- CVD equipment does not normally require ultrahigh vacuum, which simplifies the equipment and reduces its cost.
- Deposition parameters, such as temperature, flow rate, pressure, reactant concentrations can be varied in a wide range to allow many changes in composition and properties of materials deposited.

Different methods can be used to activate chemical reactions of the precursors near the substrate surface and to promote product deposition. The most important of them are [3]:

- **Thermal activation** typically requires substrate temperatures significantly higher than other methods; however, temperatures can often be considerably lowered by an appropriate choice of precursors.

- **Photon activation.** Ultraviolet radiation is used to activate precursor molecules in the gas phase.

- **Plasma activation.** Precursors are decomposed at the surface by glow discharge that can be generated by radiofrequency and microwave discharge, electron cyclotron resonance or other methods.

The latter two techniques allow for the possibility to reduce the deposition temperature considerably. However, they require complex and expensive setups and,
most importantly, only allow deposition on line-of-sight surfaces, and are thus not suitable for uniform infiltration into the 3D porous templates, such as colloidal crystals.

As with any other chemical reaction, the CVD process is governed by thermodynamics and by kinetics. Obviously, deposition can only happen when the free energy change of the reaction is negative. Most of the CVD processes are endothermic and so they require elevated substrate temperatures for the reactions to occur.

The kinetics of CVD can be relatively complex due to the fact that deposition is affected by fluid dynamics as well as the mechanism of a heterogeneous chemical reaction happening on the substrate surface. A typical CVD process can be divided into a number of individual mechanistic steps such as those schematically shown in Figure 6.2. These steps are [5]:

1. Forced flow of reactant gases into the reactor.

2. Diffusion and viscous flow of reactant gases through the gaseous concentration boundary layer to the substrate.

3. Adsorption of reactants onto the substrate.

4. Actual deposition - chemical reaction of the adsorbed species with the substrate.

5. Desorption of reaction products from the substrate.

6. Diffusion and viscous flow of product gases through the boundary layer to the bulk gas.

7. Forced exit of gases from the system.
Schematic representation of a CVD process in a viscous flow: (1) flow of reactants into reactor; (2) diffusion of reactant gases through concentration boundary layer to the substrate; (3) adsorption of reactants on the substrate; (4) chemical reaction of adsorbed species with the substrate; (5) desorption of gaseous by-products; (6) diffusion of by-products through boundary layer to bulk gas; (7) exit of gases from the reactor.

It is worth noting, that the above description applies to CVD depositions in the viscous flow range, where pressure is relatively high. If the pressure used is in the mTorr range or lower, then the concept of a boundary layer is no longer applicable.

If the conditions are such that the gas flow is laminar, then the velocity of the gas at the deposition surface equals zero. The boundary layer is then defined as the region in which the flow velocity changes from zero at the interface to the velocity of the bulk gas away from the substrate surface. The thickness of the boundary layer depends on such factors as the reactor geometry, gas pressure and flow rate.

The slowest of the seven steps shown in Figure 6.2 determines the deposition rate. Varying deposition parameters sometimes allow for a choice as to which step is rate-limiting, thus giving extra flexibility to the CVD process. For example, in order to control the rate of deposition by surface reactions one can decrease the deposition temperature
and/or reduce the gas pressure. The lower temperature will slow down the chemical reaction, while the lower pressure will lead to thinner boundary layer and faster diffusion, thus creating a surplus of reactants at the surface [3].

A CVD process in which the gaseous reactants infiltrate into a porous structure that acts as a substrate is sometimes referred to as chemical vapour infiltration (CVI). The deposition occurs on the internal surface of the 3D open porous substrate and the structure gradually becomes filled to form a non-porous composite [6]. The kinetics of the CVI process is different from the conventional line-of-sight CVD, since the reactants have to diffuse through the porous structure and the gaseous by-products have to diffuse out. Thus, the maximum degree of infiltration can be attained in the kinetically limited low-temperature, low-pressure regime.

Ideally, film growth by CVI is an omni-directional isotropic process. In such cases the infiltration occurs while voids through which gas can penetrate inside the template are open. If a silica colloidal crystal is used as a template for CVI, then the smallest voids through which the reactant gas can travel are triangular sites in the (111) planes of the f.c.c. or h.c.p. crystals [2]. As soon as these voids become closed by the shell being grown on the spheres, the reactants cannot travel into the opal and deposition ceases. Simple geometric calculations demonstrate that the maximum thickness of the shell $l_{sh}$ deposited into the close packed array of spheres equals ~0.155 of the sphere radius $r_{sph}$ (see Figure 6.3 and Equation 6.1). This means that approximately 86% of the total pore volume of the colloidal crystal can be infiltrated via surface deposition process.
A cross-sectional cut through the centres of three adjacent spheres in the (111) plane of an f.c.c. array. The deposition occurs until the growing shells close the void between the spheres.

\[ l_{sh} = AO - r_{sph} = \frac{AB}{\sqrt{3}} - r_{sph} = \left(\frac{2}{\sqrt{3}} - 1\right)r_{sph} \approx 0.155r_{sph} \]  

**Eq. 6.1.**

### 6.2.1.2. **Si CVD from silanes**

Different reactant gases and CVD reactions are available for silicon deposition. The deposited material can be either crystalline or amorphous. As discussed in Section 2.3.5.3 of this thesis, depositing amorphous silicon might be beneficial for maintaining structural integrity of the inverse silicon opal electrode during electrochemical cycling. Heating silica opals above 600 °C induces mass flow at the contact points between spheres and leads to significant shrinkage of the lattice parameter, cracking and decrease of the pore size. At the same time, it is demonstrated in the previous section that lower deposition temperatures are essential for complete and uniform CVI into a 3D porous structure. All these considerations force us to look for a silicon CVD precursor that allows deposition to occur at the lowest possible temperature.
Most precursors for silicon CVD are chlorinated silanes (silicon tetrachloride \( \text{SiCl}_4 \), trichlorosilane \( \text{SiHCl}_3 \), dichlorosilane \( \text{SiH}_2\text{Cl}_2 \)) and silanes (monosilane or silane \( \text{SiH}_4 \), and disilane \( \text{Si}_2\text{H}_6 \)). Chlorosilanes are often used for epitaxial silicon CVD, and they allow for the production of films of superior quality by reactions that can be generalised as follows:

\[
\text{SiCl}_n\text{H}_{4-n} + (n-2)\text{H}_2 \rightarrow \text{Si} + n\text{HCl}
\]

**Eq. 6.2.**

However, high temperatures, generally above 1000 °C, are required for silicon deposition from chlorosilanes [7]. Also, a highly corrosive \( \text{HCl} \) gas is formed during the reaction, which complicates the CVD reactor design.

The most commonly used precursor for silicon CVD is silane \( \text{SiH}_4 \). Thermally activated CVD can be performed over a wide range of temperatures (650 °C to 1100 °C) and pressures ranging from millitorrs to atmospheric by the following reaction [8,9]:

\[
\text{SiH}_4 \rightarrow \text{Si} + \text{H}_2
\]

**Eq. 6.3.**

Amorphous silicon can be deposited from silane at temperatures as low as 560 °C [3].

Two neighbouring dangling bonds participate in dissociative chemisorption of silane on a heated surface [10,11]. The elementary reaction of the heterogeneous monosilane decomposition can be represented by the following reaction [10-12]:

\[
\text{SiH}_4 + 2 \_ \rightarrow \text{SiH}_3 + \text{H}
\]

**Eq. 6.4,**

where the symbol \( \_ \) denotes an active centre of the surface (dangling bond), \( \text{H} \) and \( \text{SiH}_3 \) mean that \( \text{H} \) and \( \text{SiH}_3 \) are bound to the surface.

Trihydride and dihydride groups are unstable at high temperatures, so further decomposition takes place [13]:

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\[ \ce{SiH_3 + 2_\text{H} \rightarrow SiH_2 + H} \quad \text{Eq. 6.5,} \]
\[ \ce{SiH_2 + 2_\text{H} \rightarrow SiH + H} \quad \text{Eq. 6.6.} \]

Two neighbouring surface hydrides can recombine into a hydrogen molecule and desorb from the surface:
\[ 2_\text{H} \rightarrow 2_\text{H} + H_2 \quad \text{Eq. 6.7.} \]

It has been demonstrated by several research groups that disilane allows silicon deposition (Equation 6.8) at temperatures significantly lower than those required for CVD from silane [13-15]. The stoichiometry of the deposition process can be summarised as follows:
\[ \ce{Si_2H_6 \rightarrow 2Si + 3H_2} \quad \text{Eq. 6.8.} \]

The actual mechanism of disilane adsorption and decomposition is still debated. Most researchers consider the decomposition of disilane into two silicon trihydride groups to be the most probable scenario [15-17]:
\[ \ce{Si_2H_6 + 2_\text{H} \rightarrow 2SiH_3} \quad \text{Eq. 6.9.} \]

The fact that the \(Si-Si\) bond (3.5 eV) is weaker than the \(Si-H\) bond (4.0 eV) in disilane [18] seems to support the above mechanism. However, several reports suggest a different dissociation mechanism [14,19-21]:
\[ \ce{Si_2H_6 + 2_\text{H} \rightarrow SiH_2SiH_3 + H} \quad \text{Eq. 6.10.} \]

J. Shi et al. [21] in a recent report provide density functional calculations of the dissociative disilane adsorption proving that surface decomposition into two silicon
trihydride groups is sterically difficult, and that Si-H bond cleavage is more favourable kinetically. Their calculations also show that the Si-H bond in disilane cleaves more easily than Si-H bond in silane, which agrees with the earlier experimental data.

The sticking coefficient is a useful characteristic that allows for a quantification of how well species adsorb, or ‘stick’, to a surface. It is defined as a ratio of the number of adsorbate molecules that do adsorb to a surface to the total number of molecules of the same kind that impinge upon that surface [22]. In the case of silicon CVD the sticking coefficient $\varepsilon$ can be calculated as follows [23]:

$$\varepsilon = \frac{W \rho}{Z m}$$  \hspace{1cm} \text{Eq. 6.11},

where $W$ is the rate of the film growth, $\rho$ is the density of the growing silicon film, $Z$ is the collision frequency of the precursor molecules with the unit surface area; $m$ is the mass of the silicon atom.

Onischuk and Panfilov [23] summed up kinetic data on silicon deposition from silane and disilane that has been published by the year 2000 and derived the equations for the reaction sticking coefficients of silane $\varepsilon_{SiH_4}$ and disilane $\varepsilon_{Si_2H_6}$ for a wide range of temperatures and pressures:

$$\varepsilon_{SiH_4} = 10^{3.0} e^{\frac{148(kJ/mol)}{RT}} p_{SiH_4}^{0.59}$$  \hspace{1cm} \text{Eq. 6.12},

$$\varepsilon_{Si_2H_6} = 10^{1.6} e^{\frac{119(kJ/mol)}{RT}} p_{Si_2H_6}^{0.70}$$  \hspace{1cm} \text{Eq. 6.13},

where $p_{SiH_4}$ and $p_{Si_2H_6}$ are partial pressures of silane and disilane respectively.
For a deposition temperature of 450 °C, silane pressure of 2 Torr and disilane pressure of 1 Torr (conditions close to the actual Si depositions performed in this work) Equations 6.12 and 6.13 give the value of the disilane sticking coefficient to be ~4.4 times higher than that of silane. Disilane pressure used in the calculations is two times lower than the silane pressure because each disilane molecule provides two Si atoms for the growing film. This estimation confirms that disilane is a preferred reactant for the low temperature silicon CVD.

Basing on the above discussed literature data disilane gas was chosen as a precursor for syntheses of silicon inverse opals and carbon-silicon composites used in this study.

6.2.1.3. **Static CVD**

The original silicon inverse opals were synthesised via a hot-wall static CVD [1]. In such a process deposition is performed by heating a closed reactor, with precursors loaded in it beforehand. A schematic view of the static CVD system used in this study for silicon deposition is shown in Figure 6.4.
Figure 6.4.

A hot-wall static CVD set-up. The reactor with a sample inside is connected to the vacuum line and pumped down; pumping is then stopped and the reactor is isolated (valves 1 and 4 closed); the reactor is then cooled down by immersing in liquid nitrogen; a certain amount of disilane is introduced into the vacuum line through valve 3 and is subsequently condensed and frozen in the reactor (valve 1 open); the reactor is then isolated again (valves 1 and 2 closed), detached from the vacuum line and heated in a tubular furnace.
The functioning principle of this simple CVD apparatus can be summarised in several important steps and is demonstrated in Figure 6.4. A certain amount of disilane gas is condensed in the pumped and cooled by liquid nitrogen reactor. The reactor is then heated in a circular furnace. Hydrogenated amorphous silicon (a-Si:H) is deposited inside the opal pores. The thickness of silicon deposited is proportional to the amount of disilane trapped in the reactor and is independent of the furnace temperature, considering that the system is heated long enough for the reaction to complete.

The following conditions were used to synthesise silicon inverse opals by static CVD in this study:

- deposition temperature 350-390 °C,
- deposition time 48 hours,
- disilane pressure in the reactor at room temperature 270-380 Torr (600-800 Torr at the deposition temperature).

The hot-wall static CVD proved to be a convenient and reliable method of silicon inverse opal synthesis, but it provides only limited ability to control deposition parameters. The temperature used cannot be higher than ~400 °C for opals made of large spheres (890 nm in diameter in this study), otherwise a silicon overlayer forms before full infiltration is achieved. And even lower temperatures must be used for 480 nm and 250 nm spheres as the interstices between the spheres are smaller. Low decomposition temperatures significantly slow down the reaction rate and require longer deposition times, which, in turn, increase chances of air leaks into the reactor and deposition of silicon oxides. Hydrogen, the by-product of the reaction, is not evacuated from the system as in the dynamic CVD, but instead it is trapped in the reactor and its growing
concentration quenches the deposition. Furthermore, low temperature and high $H_2$ concentration both lead to higher hydrogen content in the product, somewhat reducing the quality of the a-$Si:H$ grown [24].

Another disadvantage of this method is the high consumption of disilane gas compared to a dynamic low-pressure deposition. Also, as deposition happens not only onto the sample, but also on the walls of the reactor, the reactor requires cleaning with a concentrated alkali solution after each CVD.

6.2.1.4. Dynamic CVD

Unlike the static deposition, described in the previous section, dynamic cold-wall CVD allows for a constant supply of reactant gas to reach the hot substrate as well as the simultaneous evacuation of gaseous by-products and of unreacted precursor.

Low pressure maintained in the reactor increases the mean free path of the disilane molecules in the colloidal crystal interstices before they adsorb and decompose to form silicon. This mean free path $l$ can be described by [2]:

$$l = \frac{1}{\sqrt{2\pi\sigma^2\eta}}$$

where $\sigma$ is the collision cross-section and $\eta$ is the number of molecules per unit volume. The longer mean free path in turn enables the reaction to be performed at significantly higher temperatures (up to $\sim600$ °C) without clogging the pores on the external surface of an opal. Both lower disilane pressures and higher deposition temperatures facilitate hydrogen desorption from the substrate surface, speeding up the reaction and reducing the hydrogen content in the product [3,24].
The deposition apparatus is schematically shown in Figure 6.5. The reactor is pumped to a base pressure of $10^{-7}$ Torr before the CVD reaction. The deposition substrate is then heated to the desired temperature by a General Electric pyrolytic boron nitride (PBN) heating element. The disilane gas is flown through the reactor at a certain rate. The gas is kept at room temperature until it reaches the hot substrate where it dissociatively chemisorbs and then deposits layer-by-layer forming intrinsic hydrogenated amorphous silicon ($a$-$Si:H$).
Figure 6.5.

Schematic representation of the custom-made cold-wall low-pressure dynamic CVD used in this study. Base pressure in the system is on the order of $10^{-7}$ Torr before the CVD reaction. The substrate is heated by a GE PBN heating element connected to a temperature controller. Disilane flow is controlled by a HoribaStec SEC-4400 MC mass flow controller (flow range 5 sccm) and the pressure in the system is monitored with a MKS Baratron type 626 capacitance manometer. The unreacted disilane and the hydrogen by-product are pumped out of the reactor and passed through a hot trap ($T > 700 \degree C$) to ensure disilane decomposition.

The majority of the silicon containing samples used in this study was prepared using the dynamic cold-wall CVD system. The typical deposition conditions are as follows:
• substrate temperature 450 °C,
• disilane flow rate 0.1 sccm,
• pressure in the system 900-1100 mTorr.

These particular conditions allow for silicon deposition on a flat substrate with a rate of 40-60 nm/hr. Examples of silica-silicon composites are given in Figure 6.7.

6.2.2. Silicon over-layer removal by reactive ion etching

To ensure as complete an infiltration of silicon into the opal pores as possible CVD is usually performed for a somewhat longer period of time than is actually required for infiltration, so that after full infiltration is achieved disilane continues to decompose and an overlayer of silicon is formed on the outer surface of the silica-silicon composite (Figure 6.7.a-c). This overlayer needs to be removed to ensure proper access for the HF etchant to the silica spheres (see Section 6.2.3) and, more importantly, access of electrolyte to the interior of the inverse opal during electrochemical cycling (see Section 6.3).

The overlayer removal can be achieved by different types of anisotropic etching, reactive ion etching (RIE) being one example. RIE is a plasma-based dry etching technique that can be described as a combination of physical sputtering with chemical etching activity of the reactive species. A schematic illustration of a basic RIE system is shown in Figure 6.6. The following processes take place in the system during the RIE process [25]:

• active species generation from a feed gas (e.g. CHF₃ for Si etch) by a glow discharge;
- formation of a dc bias by creating a negative charge on a high-frequency capacitatively coupled electrode at the bottom of the reaction chamber, so that material placed on the electrode is exposed to cation bombardment;
- diffusion driven transport of plasma-generated reactive species to the surface of the material being etched;
- reactive radicals ($F$ atoms) adsorb on the surface of the material to be etched (this step can be strongly enhanced by concurrent ion bombardment);
- reaction between the adsorbed species and the material to be etched takes place producing volatile species ($SiF_4$);
- desorption and pump-out of volatile reaction product.

![Figure 6.6.](image)

Schematic representation of an RIE apparatus.

Proper choice of reactant gas composition and of other etching parameters, such as RIE power, gas pressures and flow rates allow a truly unidirectional etching of the overlayer (Figure 6.7.d-f).
Specifically, all silicon overlayer etching was performed in a Trion Phantom II RIE/ICP machine. The optimal etching parameters (the fastest rate, while maintaining
maximal etching anisotropy) were found to be as follows: RIE power of 200 W, pressure of 50 mTorr, \( CHF_3 \) flow rate of 48sccm, \( O_2 \) flow rate of 2 sccm. The etching rate under these conditions is approximately 20 nm/min.

### 6.2.3. Silica template removal

After silicon CVD and overlayer removal the silica-silicon composite is converted to an inverse silicon opal. This is done by way of chemically etching the silica in aqueous 2 vol. % \( HF \) solution. The usual etching time is 8-10 hours. Figure 6.8 demonstrates some examples of amorphous silicon inverse opals. The iridescence observed on the photographs (Figure 6.8.a-b) is an indication that the structures retain their periodicity on the scale close to the wavelengths of visible light. High quality achieved during the \( Si \) deposition and the smoothness of a-\( Si:H \) coating is confirmed by SEM images (Figure 6.8.c-e). The back side of a free standing inverse opal film (Figure 6.8.f) is shown to confirm that the structure maintains its porosity and provides easy access of electrolyte all the way to the bottom.
Figure 6.8.

Photographs (a),(b) and SEM images (c)-(f) of silicon inverse opals.

It is important not to overexpose material to the etchant as a-Si:H can be etched by fluorides in the presence oxidative species (even atmospheric oxygen dissolved in the solution can be sufficient) albeit at a much slower rate than silica. Figure 6.9 demonstrates such an over etched inverse silicon opal.
6.2.4. **Characterisation of as-synthesised amorphous silicon inverse opals**

6.2.4.1. **SEM characterisation**

Scanning electron microscopy was routinely used to assess the quality of silicon inverse opals, to confirm film thickness, uniformity of silicon infiltration and the completeness of silica template removal. Such routine analyses proved to be invaluable for optimisation of the CVD and etching conditions.

6.2.4.2. **μ-Raman**

Silicon inverse opal films were characterised by Raman micro-spectroscopy (see Section 4.2.5) in the range of 195–2430 cm\(^{-1}\). The laser power was kept at 20 kW/cm\(^2\), a value considered sufficiently low so as not to cause crystallisation or other undesirable thermal transformations in amorphous hydrogenated silicon [26]. The spectra obtained closely resemble those reported in literature [27,28]. An intense peak corresponding to the first order optical phonons in silicon was used to characterise the materials. The position of this peak, its shape and width are very sensitive to the structure of silicon. Amorphous silicon produces an asymmetric peak whose maximum value is around
480 cm\(^{-1}\), while the spectra of ‘infinite’ silicon crystals (i.e., silicon crystallites larger than 10 nm [28]) have a much narrower Gaussian peak centred at 519 cm\(^{-1}\). Representative Raman spectra for silicon inverse opals synthesised via dynamic CVD at 450 °C are shown in Figure 6.10. Peak positions and full widths at half maximum (FWHM) are summarised in Table 6.1.

Raman spectra confirmed that the as-prepared silicon inverse opals were indeed amorphous. As expected, the silicon structure did not depend on the template sphere size.

![Figure 6.10.](image)

\(\mu\)-Raman spectra of amorphous silicon inverse opals. Spectral intensities are normalised.

**Table 6.1.**

<table>
<thead>
<tr>
<th>Sphere size, nm</th>
<th>Peak position, cm(^{-1})</th>
<th>FWHM, cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>480.6</td>
<td>20.7</td>
</tr>
<tr>
<td>480</td>
<td>483.0</td>
<td>22.1</td>
</tr>
<tr>
<td>890</td>
<td>480.6</td>
<td>20.1</td>
</tr>
</tbody>
</table>
6.2.4.3. **XPS**

The composition and chemical states of components on the silicon surface were studied by means of X-ray photoelectron spectroscopy. The elemental composition of a typical silicon inverse opal film is presented in Table 6.2:

**Table 6.2.**

Elemental composition of the surface of a silicon inverse opal as obtained by XPS. The composition of native oxide on silicon [29] is provided for comparison.

<table>
<thead>
<tr>
<th>Element</th>
<th>Silicon inverse opal</th>
<th>Native oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>39.7</td>
<td>42</td>
</tr>
<tr>
<td>O</td>
<td>28.7</td>
<td>32</td>
</tr>
<tr>
<td>F</td>
<td>14.3</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>17.3</td>
<td>25</td>
</tr>
</tbody>
</table>

The elemental composition of the silicon inverse opal was very similar to the composition of native oxide on pure silicon [29] with one exception – a significant amount of fluorine was present on the surface of silicon inverse opals. Fluorine could have been introduced during HF treatment, and, together with carbon, during the RIE with $CHF_3$.

XPS spectra of individual elements are shown in Figure 6.11. The silicon 2p signal has two well defined components: the peak at 99.3 eV arises from $Si-Si$ bonding, while the broad peak at 104 eV originates from $Si-O$ and $Si-F$ bonds. A very broad and complex carbon 1s peak, together with the fact that the carbon content is lower than found on surfaces of native silicon oxide, suggests that most of the carbon is introduced by contamination from air, rather than by a polymerisation reaction during RIE.
Figure 6.11.

XPS spectra of an amorphous silicon inverse opal: (a) Si 2p, (b) O 1s, (c) F 1s, (d) C 1s.

6.2.4.4. TGA

Amorphous silicon inverse opals were characterised by thermogravimetric analysis. Finely ground inverse opal films were heated from room temperature to 1400 °C at the rate of 2 °C/min in air in order to oxidise all of the silicon:

$$Si + O_2 \rightarrow SiO_2$$  \hspace{1cm} \text{Eq. 6.15.}

The TGA curve of the silicon inverse opals is shown in Figure 6.12. After an initial weight loss of about 0.5 % due to evaporation of water and other volatile species, the weight of the material was stable until approximately 550 °C. From this temperature on the weight consistently increased until 1200 °C. Interestingly, two distinct steps are observed on the curve. The first sharp weight increase is finished by about 800 °C, while
the second, much smaller step is located between 850 °C and 1200 °C. One possible explanation for such behaviour is that some of the amorphous silicon crystallises before being oxidised, thus requiring higher temperatures to complete its oxidation.

![TGA profile of silicon inverse opals in air.](image)

**Figure 6.12.**

TGA profile of silicon inverse opals in air.

Complete conversion of pure silicon to silicon dioxide should increase the weight of the material by 113.9 %. In the case of silicon inverse opals a lower weight increase of 103.4 % was observed (the values at 200 °C, after the completion of low temperature weight loss, and at 1300 °C were used for calculations). This indicates that the material contains significant amounts of oxygen. Assuming that oxygen is the only impurity present, the elemental composition of the inverse opals can be calculated as follows:

\[ x_{Si} + x_{O} = 100\% \]  \hspace{1cm}  \text{Eq. 6.16,}

\[ \frac{x_{Si} + x_{O} + x^{add}}{x_{Si} + x_{O}} = \frac{m_{200}}{m_{1300}} \]  \hspace{1cm}  \text{Eq. 6.17,}

\[ \frac{x_{Si}}{x_{O} + x^{add}} = \frac{M_{Si}}{2M_{O}} \]  \hspace{1cm}  \text{Eq. 6.18,}
where \( x_{Si} \) and \( x_{O} \) are the weight fractions of silicon and oxygen in the initial material, \( x_{add} \) is the weight fraction added during oxidation, \( m_{200} \) and \( m_{1300} \) are weights at 200 °C and at 1300 °C respectively, \( M_{Si} \) and \( M_{O} \) are the atomic weights of silicon and oxygen.

The weight fractions of silicon and oxygen calculated using Equations 6.16-6.18 are 95.1 wt.% and 4.9 wt.% respectively. It should be noted, that in practice the oxygen content can be somewhat lower due to presence of other impurities. If the oxidation of these impurities happens in the same temperature range as formation of silicon dioxide, then the weight loss caused by formation of their volatile oxidation products has been wrongly attributed to the presence oxygen in the initial material.

6.2.4.5. **XRD**

Silicon inverse opals were studied by powder X-ray diffraction. For this purpose several films were ground together and XRD analysis was performed using a Siemens/Bruker AXS D5000 diffractometer with the 2\( \Theta \) angle ranging from 10° to 70°. Two broad low intensity peaks with maxima around 28° and 51° were observed. This pattern is typical of amorphous silicon [30].

![PXRD pattern of an amorphous silicon inverse opal.](image)

**Figure 6.13.**

PXRD pattern of an amorphous silicon inverse opal.
6.2.4.6. **Conductivity measurements**

The conductance of silicon inverse opals was measured by two-probe method as described in Section 4.2.8. The measured conductivities varied in the range of $6 \cdot 10^{-7}$ S/cm to $4 \cdot 10^{-6}$ S/cm. These values are relatively high, considering that most of the reported conductivities of hydrogenated amorphous silicon are $10^{-8}$ S/cm or less [31]. An increase in conductivity can be explained by combination of factors including high deposition temperature and hence lower hydrogen content, and relatively high level of oxygen, which is known to increase the room temperature conductivity of amorphous silicon [32].

6.2.5. **Conversion of amorphous hydrogenated silicon to crystalline form**

Electrochemical performance of inverse opals composed of nanocrystalline silicon was also studied (see Section 6.3.2). For this purpose silicon inverse opals were prepared as described in the previous sections and were then heated to 800 °C in argon or nitrogen atmosphere for 12 hours.

6.2.6. **Characterisation of crystalline silicon inverse opals**

6.2.6.1. **SEM characterisation**

SEM images of a silicon inverse opal film after crystallisation are shown in Figure 6.14. In contrast to the smooth surface of amorphous silicon (Figure 6.8) the crystalline samples had a rough ‘grainy’ structure. The size of the grains was estimated to be on the order of few tens of nanometres.
6.2.6.2. $\mu$-Raman

Raman micro-spectroscopy of crystallised silicon inverse opals was performed in the same way as in the case of amorphous samples. A typical spectrum, obtained from the crystalline silicon inverse opal templated from 480 nm spheres, is presented in Figure 6.15 and Table 6.3. The spectrum of the amorphous material is shown for comparison.

The crystallised samples produced a highly symmetric narrow peak with a maximum around 520 cm$^{-1}$, and no shoulder or amorphous peak at 480 cm$^{-1}$ was observed. This indicates that temperature annealing of silicon inverse opals produced a fully crystalline material with crystallite sizes exceeding 10 nm [28].
Figure 6.15.

μ-Raman spectra of crystalline and amorphous silicon inverse opals. Spectra intensities are normalised.

Table 6.3.

Peak positions and full widths at half maximum for the spectra presented in Figure 6.15.

<table>
<thead>
<tr>
<th></th>
<th>Peak position, cm⁻¹</th>
<th>FWHM, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous silicon</td>
<td>483.0</td>
<td>22.1</td>
</tr>
<tr>
<td>Crystalline silicon</td>
<td>521.4</td>
<td>7.4</td>
</tr>
</tbody>
</table>

6.2.6.3. XPS

The XPS spectra of crystalline silicon inverse opal are shown in Figure 6.16 and the elemental composition is shown in Table 6.4. The annealing of silicon inverse opal films lead to the elimination of fluorine from the material surface, probably via desorption of volatile fluorides. At the same time, an increase in oxygen content compared to amorphous silicon was observed. The proportion of silicon-oxygen bonds in comparison to silicon-silicon was also increased. The C 1s spectrum closely resembles the one observed in amorphous silicon (Figure 6.11.d), further indicating that ambient atmosphere is the major source of carbon contamination in both cases. Overall, the composition is similar to the composition of the native oxide on silicon [29].
Table 6.4.
Elemental composition of crystalline silicon inverse opal surface obtained by XPS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Content, at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>43.3</td>
</tr>
<tr>
<td>O</td>
<td>37.1</td>
</tr>
<tr>
<td>F</td>
<td>0.0</td>
</tr>
<tr>
<td>C</td>
<td>19.6</td>
</tr>
</tbody>
</table>
Figure 6.16.

XPS spectra of a crystalline silicon inverse opal: (a) Si 2p, (b) O 1s, (c) C 1s.

6.2.6.4. **XRD**

PXRD data of annealed silicon inverse opals was collected on a Siemens/Bruker AXS D5000 diffractometer with 2Θ ranging from 18° to 90° as described in Section 4.2.6. The XRD pattern shown in Figure 6.17 confirms that annealing resulted in crystalline silicon.
Peak broadening is an indication of relatively small crystallites, and it can be used for estimation of the particle size. The three largest peaks were chosen for calculations of the silicon crystallite size. Calculations were performed by direct peak profile deconvolution using the Topas™ software. Multiple profile fittings of the selected peaks were done to establish the standard deviation. Results obtained from all peaks were relatively close to each other being in the range of 34-42 nm; they are summarised in Table 6.5.

Table 6.5.
Crystallite sizes calculated from XRD peak broadening.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Crystallite size, nm</th>
<th>Standard deviation, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>40.7</td>
<td>1.2</td>
</tr>
<tr>
<td>220</td>
<td>34.6</td>
<td>3.8</td>
</tr>
<tr>
<td>311</td>
<td>41.5</td>
<td>2.4</td>
</tr>
</tbody>
</table>
6.2.6.5. **Conductivity measurements**

The conductivity of nanocrystalline silicon inverse opal films measured by a two-probe method varied in the range of $7 \cdot 10^{-4}$ to $2 \cdot 10^{-3}$ S/cm. This is three orders of magnitude higher than the conductivity of amorphous silicon inverse opals.

6.3. **Electrochemical Performance of Silicon Inverse Opal Film Electrodes**

6.3.1. **Amorphous silicon**

6.3.1.1. **Cyclic Voltammetry**

Cyclic voltammetry plots of 5 µm thick silicon inverse opal films templated from silica opals composed of 250 nm, 480 nm and 890 nm spheres are shown in Figure 6.18. The cells were cycled between 2 V and 50 mV vs. Li/Li$^+$ at the scan rate of 0.1 mV/sec.
Figure 6.18.

CV curves of amorphous silicon inverse opal electrodes. Film thickness ~5 μm. Scan rate 0.1 mV/sec; scan range 0.05 – 2 V vs. Li/Li⁺ (0.05 – 1.5 V shown). Inverse opals were templated from 250 nm (a), 480 nm (b), and 890 nm (c) spheres.

The shapes of CV curves are consistent with the results previously reported in literature for nanostructured silicon anodes [33-35]. The lithiation process occurs at potentials below 0.3 V, while de-lithiation is mostly completed before voltage reaches the
value of 0.6 V. The positions and relative intensities of cathodic (lithiation) and anodic (de-lithiation) peaks are summarised in Table 6.6. In addition to the peaks listed in Table 6.6 a small peak or ‘bump’ is observed around 0.26-0.29 V during lithiation process.

Table 6.6.

Peak positions and relative intensities for cyclic voltammograms presented in Figure 6.10.

<table>
<thead>
<tr>
<th>Sphere size, nm</th>
<th>Cycle #</th>
<th>Cathodic peak</th>
<th>Anodic peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Peak position, V</td>
<td>Relative intensity of value at 0.05 V to peak value</td>
</tr>
<tr>
<td>250</td>
<td>1</td>
<td>-</td>
<td>2.04*</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.20</td>
<td>1.47</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.20</td>
<td>1.53</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.20</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.20</td>
<td>1.55</td>
</tr>
<tr>
<td>480</td>
<td>1</td>
<td>-</td>
<td>2.15*</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.20</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.20</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.20</td>
<td>1.21</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.20</td>
<td>1.18</td>
</tr>
<tr>
<td>890</td>
<td>1</td>
<td>-</td>
<td>2.07*</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.20</td>
<td>1.14</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.20</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.20</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.20</td>
<td>1.13</td>
</tr>
</tbody>
</table>

* Relative intensity of value at 0.05 V to value at 0.20 V.
The shape of the curve corresponding to the first cycle differs essentially from the subsequent ones. The onset of lithiation during the first cycle happened later, this effect being most evident in the case of 890 nm spheres. The cathodic peak at 0.20 V is much less pronounced during the first cycle. Interestingly, the first anodic peak has a lower intensity and is significantly shifted towards higher voltages during the first cycle, while the second peak is similar in shape and position to the later cycles. Similar effects have been observed previously [33,35,36]. The reason for such behaviour is not exactly clear, however, it can be conjectured that some sort of local restructuring or ‘activation’ takes place in silicon during the initial lithium alloying.

After the first cycle, scans assume remarkably repeatable shapes suggesting high reversibility of lithiation-delithiation reaction. It is worth noting that anodic peaks are better separated from each other in the case of electrodes templated from smaller spheres. The position of the first anodic peak shifts slightly towards higher voltages with increasing sphere size, while the position of the second de-lithiation peak, though determined with less accuracy due to peak overlapping, is almost intact. This suggests that the rate of the reaction in the early stages of de-lithiation was to some extent controlled by the rate of solid-state lithium diffusion in the electrode material, so that thicker walls caused larger polarisation.

6.3.1.2. **Galvanostatic cycling**

The cycling behaviour of silicon inverse opal film electrodes has been studied by galvanostatic cycling of coin cells described in Section 4.3.3 between 0.05 V and 2 V vs. \( \text{Li/Li}^+ \) at current rates ranging from C/10 to 10C. The sequence of current rates applied is
summarised in Table 6.7. C rates have been calculated based on the theoretical capacity of 3579 mAh/g corresponding to the $Li_{15}Si_4$ phase.

**Table 6.7.**
The sequence of C rates during galvanostatic cycling.

<table>
<thead>
<tr>
<th>Cycle #</th>
<th>C/10</th>
<th>C/5</th>
<th>C/2</th>
<th>1C</th>
<th>2C</th>
<th>5C</th>
<th>10C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-25</td>
<td>36-45</td>
<td>56-65</td>
<td>76-85</td>
<td>96-105</td>
<td>116-125</td>
<td>136-145</td>
<td>126-135</td>
</tr>
</tbody>
</table>

The performance of 5 and 10 $\mu$m thick inverse opal films prepared from 250 nm spheres; 5, 10 and 15 $\mu$m thick films from 480 nm spheres; 5, 10 and 15 $\mu$m thick films from 890 nm spheres has been studied. The cycling behaviour of these electrodes is demonstrated in Figures 6.19-6.21 and some significant features are shown in Table 6.8.
Figure 6.19.

Galvanostatic cycling of amorphous silicon inverse opal electrodes templated from 250 nm spheres:

(a) Cycling behaviour of 5 μm film; (b) charge transferred – voltage curves for selected cycles of 5 μm film; (c) cycling behaviour of 10 μm film; (d) charge transferred – voltage curves for selected cycles of 10 μm film.
Figure 6.20.

Galvanostatic cycling of amorphous silicon inverse opal electrodes templated from 480 nm spheres:

(a) Cycling behaviour of 5 μm film; (b) charge transferred – voltage curves for selected cycles of 5 μm film; (c) cycling behaviour of 10 μm film; (d) charge transferred – voltage curves for selected cycles of 10 μm film; (e) cycling behaviour of 15 μm film; (f) charge transferred – voltage curves for selected cycles of 15 μm film.
Galvanostatic cycling of amorphous silicon inverse opal electrodes templated from 890 nm spheres:

(a) Cycling behaviour of 5 μm film; (b) charge transferred – voltage curves for selected cycles of 5 μm film; (c) cycling behaviour of 10 μm film; (d) charge transferred – voltage curves for selected cycles of 10 μm film; (e) cycling behaviour of 15 μm film; (f) charge transferred – voltage curves for selected cycles of 15 μm film.
Most electrodes demonstrated initial delithiation capacities over 2500 mAh/g (Table 6.8), which, though lower than the theoretical value, are comparable to the values for nanostructured silicon anodes reported in literature [33-36].

Low coulombic efficiencies, lying in the range of 65 to 87 %, and hence high irreversible capacities during the first cycle can be caused by several side processes, namely by formation of solid-electrolyte interphase (SEI), by the irreversible reaction of lithium with the dangling bonds in silicon, which are known to have a strong affinity towards lithium, and by the reaction of lithium with surface oxides and fluorides, leading to the formation of \( \text{Li}_2\text{O} \) and \( \text{LiF} \) respectively. Interestingly, initial coulombic efficiencies increased with the increase of sphere diameter. This, together with the fact that surface to volume ratio of an inverse opal material is inversely proportional to the diameter of templating spheres, is a further indication that irreversible capacities during the first galvanostatic cycles arise from processes on the electrode surfaces. Coulombic efficiencies increased during the first 3-5 cycles eventually reaching levels over 97 %.

Electrodes prepared from 890 nm spheres demonstrated better cycling stability, with their capacity retentions being around 70 % after 145 cycles, compared to 55 % for 480 nm spheres and 50 % or lower in the case 250 nm spheres. It can be conjectured that smaller pores of the latter materials are more easily blocked or ‘clogged’ by the swelling electrode material during lithiation, preventing penetration of the electrolyte and thus gradually excluding more and more material from the electrochemical reaction (see Figure 6.24). A similar effect has been observed by Stein and colleagues for tin oxide inverse opal electrodes [37].
Table 6.8.

Cyclic performance of amorphous silicon inverse opals: initial capacities and coulombic efficiencies; capacity retentions and coulombic efficiencies after 25 and 145 galvanostatic cycles.

<table>
<thead>
<tr>
<th>Cycle #</th>
<th>Sphere size, nm</th>
<th>250</th>
<th>480</th>
<th>890</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Film thickness, μm</td>
<td>5</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>1</td>
<td>De-lithiation capacity, mAh/g</td>
<td>2829</td>
<td>2469</td>
<td>2069</td>
</tr>
<tr>
<td></td>
<td>Coulombic efficiency, %</td>
<td>76.0</td>
<td>70.3</td>
<td>65.2</td>
</tr>
<tr>
<td>25</td>
<td>Capacity retention, %</td>
<td>74.5</td>
<td>74.6</td>
<td>80.7</td>
</tr>
<tr>
<td></td>
<td>Coulombic efficiency, %</td>
<td>98.1</td>
<td>97.4</td>
<td>97.4</td>
</tr>
<tr>
<td>145</td>
<td>Capacity retention, %</td>
<td>50.5</td>
<td>16.2</td>
<td>56.7</td>
</tr>
<tr>
<td></td>
<td>Coulombic efficiency, %</td>
<td>98.1</td>
<td>93.6</td>
<td>97.3</td>
</tr>
</tbody>
</table>

* Data for cycle 139.

The rate performance of amorphous silicon inverse opal electrodes is further outlined in Table 6.9 and Figure 6.22. Capacities decreased exponentially with the increase of current, reaching negligible values before or at 1C rate. No apparent correlation of rate performance with the sphere size can be observed, suggesting that lithium diffusion is not a rate-limiting process. On the other hand, thinner films demonstrated better performance at high currents, which indicates that the rate of lithium alloying-dealloying is controlled by electrical conductivity of the electrode material.
Table 6.9.
Rate performance of amorphous silicon inverse opal electrodes: de-lithiation capacities and coulombic efficiencies at different current rates.

<table>
<thead>
<tr>
<th>Cycle #</th>
<th>C rate</th>
<th>Sphere size, nm</th>
<th>250</th>
<th>480</th>
<th>890</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Film thickness, μm</td>
<td>5</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>20</td>
<td>C/10</td>
<td>Capacity, mAh/g</td>
<td>2134</td>
<td>1871</td>
<td>1697</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>98.0</td>
<td>97.5</td>
<td>97.4</td>
</tr>
<tr>
<td>30</td>
<td>C/5</td>
<td>Capacity, mAh/g</td>
<td>1499</td>
<td>1200</td>
<td>1175</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>98.2</td>
<td>97.4</td>
<td>97.3</td>
</tr>
<tr>
<td>50</td>
<td>C/2</td>
<td>Capacity, mAh/g</td>
<td>702</td>
<td>338</td>
<td>538</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>97.8</td>
<td>97.3</td>
<td>97.2</td>
</tr>
<tr>
<td>70</td>
<td>1C</td>
<td>Capacity, mAh/g</td>
<td>136</td>
<td>48</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>97.8</td>
<td>95.5</td>
<td>97.1</td>
</tr>
</tbody>
</table>

Figure 6.22.
Rate performance of amorphous silicon inverse opal electrodes: de-lithiation capacities at different current rates (Data from Table 6.9).
6.3.1.3. **Physical characterisation of cycled material**

**SEM characterisation**

The silicon inverse opal electrodes after electrochemical cycling were studied by scanning electron microscopy. The sample preparation technique that allowed avoiding exposure of electrodes to atmosphere is described in Section 4.2.2. In brief, electrochemical cells were disassembled in an argon-filled glove box, the electrode material was washed, transferred onto the sample holder, and then loaded into the SEM machine through an argon-filled glove bag attached to SEM inlet port.

SEM imaging of materials after five slow (0.1 mV/sec) CV scans revealed significant morphological changes in the structure of silicon inverse opal electrodes (Figure 6.23). The cycled materials had an interesting ‘sponge-like’ structure. Importantly, even though the morphology was very different from the un-cycled material (Figure 6.8) the structure was still porous and open to electrolyte.
Figure 6.23.
Amorphous silicon inverse opals after cyclic voltammetry. (a),(b) Templated from 250 nm spheres; (c),(d) templated from 480 nm spheres; (e),(f) templated from 890 nm spheres.

Morphology changes occurring at different degrees of lithiation were also visualised by SEM. For this purpose electrodes were cycled galvanostatically at C/10 rate.
in the range between 2 V and 50 mV for twenty cycles. Cycling was then stopped during the lithiation half-cycle of cycle 21 at 2 V (at the end of the 20\textsuperscript{th} cycle), 100 mV and 50 mV (at the end of lithiation), electrodes were prepared as discussed above and then used for electron microscopy. SEM images of 10 \mu m thick electrodes obtained from 890 nm microspheres at different degrees of lithiation are shown in Figure 6.24. Table 6.10 summarises lithium contents in the structures presented in Figure 6.24.

De-lithiated structures closely resembled pristine silicon inverse opals, indicating high reversibility of electrochemical lithium insertion. Partially lithiated electrodes had thicker walls and smaller pores between the air spheres; the structures, however, remained highly open and accessible to electrolyte. The walls of electrodes fully loaded with lithium were very thick, and virtually no macroporosity was observed.

**Table 6.10.**

Composition of electrode materials at different degrees of lithiation used for SEM imaging.

<table>
<thead>
<tr>
<th>Voltage, V</th>
<th>Charge transferred in comparison with charge at full lithiation in cycle 20, %</th>
<th>x in Li\textsubscript{x}Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.10</td>
<td>43.7</td>
<td>1.03</td>
</tr>
<tr>
<td>0.05</td>
<td>99.7</td>
<td>2.32</td>
</tr>
</tbody>
</table>
The structures of electrodes that had completely lost their capacities towards lithium as a result of prolonged galvanostatic cycling are shown in Figure 6.25. They
looked similar to the materials at maximum degree of lithiation (Figure 6.24.e-f) having very thick walls and zero porosity. It can be speculated that the cycling performance of amorphous silicon inverse opal electrodes degraded mostly due to progressive blockage of macropores by lithiated silicon, which then prevented access of electrolyte to parts of the material and excluded those parts from electrochemical reaction.
Amorphous silicon inverse opals after complete loss of cycling ability. Structures were templated from

(a) 250 nm spheres, (b) 480 nm spheres, (c) 890 nm spheres.

An interesting change in mechanical properties of cycled inverse silicon opals was also observed by SEM. Pristine inverse silicon opals are brittle and non-flexible.
This property was often used to create fresh cross-sectional areas for SEM imaging by gentle crushing of a film on the SEM holder with spatula. This simple technique applied to cycled delithiated inverse opals led to a bending of material rather than to breaking it (Figure 6.26). A similar behaviour of silicon was reported by Rogers and colleagues [38].

![Image](image.png)

**Figure 6.26.**
Flexible silicon inverse opal electrodes.

**μ-Raman**

Raman micro-spectroscopy of amorphous silicon inverse opal electrodes after electrochemical cycling was used to evaluate changes in the structure of the material caused by lithium insertion and removal. Electrochemically cycled silicon inverse opal electrodes used for μ-Raman spectroscopy were protected from atmosphere as described in Section 4.2.5. The spectrum of silicon inverse opal film templated from 480 nm silica spheres after twenty galvanostatic cycles at C/10 rate is shown in Figure 6.27, peak position and FWHM are given in Table 6.11. The spectrum of the same film before cycling is included as a reference.

Similar to the as-prepared amorphous material, the spectra obtained from electrochemically delithiated silicon demonstrate broad asymmetric first order phonon
peaks. However, these peaks are slightly shifted towards higher frequencies. Such behaviour probably arises from residual mechanical stress originally induced in the material by volume swings during electrochemical cycling. Compressive stresses in silicon are known to result in the shift the Raman peak to higher wavenumbers [39].

Figure 6.27.

μ-Raman spectra of 480 nm amorphous silicon inverse opal before and after 10 galvanostatic cycles.

Spectra intensities are normalised.

Table 6.11.

<table>
<thead>
<tr>
<th></th>
<th>Peak position, cm⁻¹</th>
<th>FWHM, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before cycling</td>
<td>483.0</td>
<td>22.1</td>
</tr>
<tr>
<td>After cycling</td>
<td>490.3</td>
<td>21.1</td>
</tr>
</tbody>
</table>

6.3.2. Nano-crystalline silicon

6.3.2.1. Cyclic voltammetry

Cyclic voltammetry of 10 μm thick crystalline silicon inverse opal films templated from 250 nm, 480 nm and 890 nm silica spheres was performed with the same parameters as the CV of amorphous silicon electrodes, namely in the voltage range
between 2 V and 50 mV vs. \( \text{Li/Li}^+ \) and at the scan rate of 0.1 mV/sec. Cyclic voltammetry plots are shown in Figure 6.28, peak positions and relative intensities are summarised in Table 6.12.

**Figure 6.28.**

CV curves of nano-crystallyne silicon inverse opal electrodes. Film thickness ~10 μm. Scan rate 0.1 mV/sec; scan range 0.05 – 2 V vs. \( \text{Li/Li}^+ \) (0.05 – 1.5 V shown). Inverse opals are templated from 250 nm (a), 480 nm (b), and 890 nm (c) spheres.
Table 6.12.
Peak positions and relative intensities for cyclic voltammograms presented in Figure 6.16.

<table>
<thead>
<tr>
<th>Sphere size, nm</th>
<th>Cycle #</th>
<th>Cathodic peak</th>
<th>Anodic peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Peak position, V</td>
<td>Relative intensity of value at 0.05 V to peak value</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-</td>
<td>0.33 0.42 0.48 1.01 1.25</td>
</tr>
<tr>
<td>250</td>
<td>2</td>
<td>0.21</td>
<td>2.11 0.33 0.42 0.46 1.23 1.28</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.20</td>
<td>1.52 0.33 - 0.48 - 1.26</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.20</td>
<td>1.56 0.33 - 0.48 - 1.25</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.20</td>
<td>1.55 0.34 - 0.48 - 1.26</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-</td>
<td>0.33 0.42 0.48 1.04 1.25</td>
</tr>
<tr>
<td>480</td>
<td>2</td>
<td>0.21</td>
<td>2.57 0.33 0.42 0.48 1.31 1.32</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.20</td>
<td>1.50 0.33 - 0.48 - 1.28</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.20</td>
<td>1.61 0.33 - 0.48 - 1.28</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.20</td>
<td>1.55 0.33 - 0.48 - 1.26</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-</td>
<td>0.32 0.43 0.48 0.87 1.33</td>
</tr>
<tr>
<td>890</td>
<td>2</td>
<td>0.20</td>
<td>2.49 0.33 0.43 0.48 1.18 1.33</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.20</td>
<td>1.53 0.33 - 0.48 - 1.27</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.20</td>
<td>1.55 0.33 - 0.48 - 1.28</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.20</td>
<td>1.43 0.33 - 0.48 - 1.26</td>
</tr>
</tbody>
</table>

* Relative intensity of value at 0.05 V to value at 0.20 V.

The shapes of crystalline silicon cyclic voltammograms resemble the CV curves of amorphous silicon electrodes (Figure 6.18 and Table 6.6), especially during later cycles, which is to be expected since the electrode material becomes amorphous upon lithiation [30]. However, there are some striking differences between two sets of data.
Firstly, in case of crystalline silicon, the cathodic process was very intensive at low voltages during the first and, to some extent, the second cycle, with the currents at 50 mV being 10-20 times higher than the currents at 200 mV, comparing to the ratio of about 2 for amorphous electrodes.

Secondly, an additional anodic peak appeared around 0.42-0.43 V during the first two cycles. This peak is quite unusual for nanostructured silicon electrodes, but a similarly positioned peak, or the corresponding plateau in galvanostatic process, was observed during de-lithiation of large silicon particles or thick silicon films. The peak has been attributed to de-lithiation of $Li_4Si_{15}$ [30,40,41], the phase that usually forms only if the material is cycled at voltages below 50 mV. None of the conditions previously considered necessary for observation of the peak at 0.42 V are met in the case of crystalline silicon inverse opals: XRD results presented in Section 6.2.6.4 suggest that the silicon crystallites were small, below 50 nm in diameter, and the material was not exposed to voltages below 50 mV vs. $Li/Li^+$. Clearly, there is an unknown factor that promotes formation of crystalline $Li_4Si_{15}$, or some other undefined phase responsible for the peak, at relatively high voltages from nano-crystalline silicon, since the characteristic peak disappeared after two CV cycles and no such peaks were observed during cycling of amorphous silicon inverse opals. Further investigation of this phenomenon is needed.

Thirdly, unlike the case of amorphous silicon, the positions of anodic peaks did not correlate with the template sphere size, suggesting either higher lithium mobility in the electrode material or shorter diffusion lengths. Shorter lithium diffusion lengths can arise from the fact that electrolyte has access to the bulk of the electrode material due to the particulate nature of the latter (Figure 6.14).
Lastly, and most importantly from the practical point of view, the current intensity decreased sharply with each cycle (Table 6.13 and Figure 6.29), suggesting that some irreversible structural changes occurred during cycling which lead to diminution of electrode material available for electrochemical reaction.

Table 6.13.
Change in the first anodic peak intensities with the cycle number.

<table>
<thead>
<tr>
<th>Cycle #</th>
<th>Sphere size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>250</td>
</tr>
<tr>
<td>1</td>
<td>1221</td>
</tr>
<tr>
<td>2</td>
<td>947</td>
</tr>
<tr>
<td>3</td>
<td>627</td>
</tr>
<tr>
<td>4</td>
<td>420</td>
</tr>
<tr>
<td>5</td>
<td>241</td>
</tr>
</tbody>
</table>

Figure 6.29.
Change in the first anodic peak intensities with the cycle number.
6.3.2.2. **Galvanostatic cycling**

In order to test the cycling performance of nano-crystalline silicon inverse opal electrodes 10 μm thick films templated from 480 nm silica spheres were cycled vs. metallic lithium in the coin cells at various current rates (Figure 6.30). The electrodes demonstrated high initial capacities combined with relatively high coulombic efficiencies even at 10C rate, probably due to much higher electronic conductivity of crystalline silicon in comparison with the amorphous one. However, capacities faded fast reaching negligible values by the 15th cycle at best. This is in agreement with the fast capacity fading observed in the CV experiments.
Figure 6.30.

Galvanostatic cycling of 10 μm nano-crystalline silicon inverse opal electrodes templated from 480 nm spheres: (a) cycling at C/10 rate; (b) cycling at 1C rate; (c) cycling at 10C rate.
6.3.2.3. **Physical characterisation of cycled material**

**SEM characterisation**

SEM images of crystalline silicon inverse opals after five CV scans at 0.1 mV/sec electrochemical cycling are presented in Figure 6.31. The material retained the structure of the inverse opal, but the ‘grains’ became larger than in crystalline silicon before cycling, suggesting incomplete lithium removal.

![SEM images of crystalline silicon inverse opals after five CV scans](image)

**Figure 6.31.**

Crystalline silicon inverse opals after five CV scans.

Figure 6.32 presents SEM images of crystalline silicon inverse opal electrode after twenty galvanostatic cycles at C/10 rate. At this point the electrode had negligible capacity (Figure 6.30.a). The electrode material had completely degraded into separate visually unstructured islands, and no traces of inverse opal structure can be found. Such a striking difference from amorphous electrodes can be explained by the fact that the silicon nano-crystallites were only weakly attached to each other and easily separated from the macroporous network under the mechanical stress caused by lithiation-delithiation.
6.4. Conclusions

High quality inverse silicon opals were prepared using silica templates by the CVD method from disilane gas. Both amorphous hydrogenated silicon and nanocrystalline silicon structures were made and characterised by such techniques as SEM, μ-Raman spectroscopy, XPS, XRD, thermogravimetric analysis and conductivity measurements.

Electrochemical cycling of silicon inverse opals revealed striking differences in the behaviour of amorphous and crystallised structures. On the one hand amorphous materials demonstrated decent capacity retentions of 50 to 70% after 145 galvanostatic cycles, but poor high current performance with virtually zero capacities already at a 1C rate. Crystalline silicon, on the other hand, had initial capacities of over 1500 mAh/g even at a 10C rate, but showed very poor cycling performance with capacities fading to negligible values by the 15th cycle. Morphological and structural changes in cycled materials were revealed by means of SEM and μ-Raman spectroscopy.
6.5. References


[29] Data from http://www.xpsdata.com/xpsdata.htm


CHAPTER 7.
SYNTHESIS AND ELECTROCHEMICAL CHARACTERISATION OF CARBON INVERSE OPAL FILMS

7.1. Preamble

The first syntheses of carbon inverse opals were reported by Zakhidov et al. in the year 1998 [1]. Three synthetic methods were implemented to fabricate three different allotropes of carbon. Glassy carbon was prepared by infiltration of furfuryl-based phenolic resin into the pores of silica opal and carbonising it in argon at 900 °C to 1000 °C. Graphitisable carbon inverse opals were synthesised by atmospheric pressure CVD at 800 °C using propylene gas in nitrogen as a precursor. Finally, diamond inverse opal films were grown by means of plasma enhanced CVD onto diamond seeds from hydrogen/methane mixture.

Since then numerous reports describing the syntheses of graphitic and amorphous carbon inverse opals or related porous structures have been published [2-15]. A variety of methods were used to introduce carbonaceous material in the pores, including CVD from benzene [10], methane [11], acetonitrile [13]; infiltration and subsequent polymerisation of divinylbenzene [5], mesophase pitch [4,14], sugars (sucrose [2,3,6], glucose [6]) and phenolic resins [7,9,12,13,15].

A detailed description of methods used in this study to fabricate carbon inverse opal films and to characterise them is presented in this chapter. The general synthetic
procedure is depicted in Figure 7.1. It includes the following steps: infiltration of a silica opal with a precursor solution, polymerisation and carbonisation of the precursor (see Section 7.2.2 for details), and structure inversion by HF etching of silica spheres (Section 7.2.3). The so obtained inverse opals were characterised (Section 7.3) by SEM, μ-Raman spectroscopy, XPS, XRD, TGA and conductivity measurements.

![Figure 7.1.](image)

General procedure for carbon inverse opal fabrication includes the following steps: infiltration of silica opal with sucrose solution and carbonisation in inert atmosphere (1), silica template removal with HF etching (2).

The results of electrochemical cycling of carbon inverse opal films are shown in Section 7.4. Their performance was studied by cyclic voltammetry at a 0.1 mV/sec scan rate and by galvanostatic cycling at varying current rates. The results of the CV tests are discussed in Section 7.4.1. Section 7.4.2 deals with the performance of carbon inverse opals cycled under galvanostatic conditions. SEM and μ-Raman characterisation of materials after cycling is discussed in Section 7.4.3.

7.2. Fabrication of Carbon Inverse Opals

7.2.1. Introduction

As was previously discussed in Section 2.3.5.1 carbonaceous materials employed as electrode materials in lithium batteries can be broadly divided into three types [16]:
• graphitic carbons,
• soft or graphitisable carbons,
• and hard, non-graphitisable carbons.

Graphitic carbons are widely used in commercial Li-ion cells. They demonstrate
good cycling stability, have relatively low irreversible capacity during the first cycle and
operate at low voltages, with lithium deintercalation mostly happening below 0.3 V vs.
$Li/Li^+$. However, their specific capacity is limited to 372 mAh/g, corresponding to
$LiC_6$ [16,17]. Graphitic carbons can be prepared by the graphitisation of soft carbons at
temperatures exceeding 2000 °C [17].

Soft carbons are those that can be synthesised by carbonisation from a variety of
precursors, including petroleum and coal-tar pitches, polyvinyl chloride, and
polyaromatic hydrocarbons [17]. Soft carbons have specific capacities exceeding
550 mAh/g when carbonised at temperatures near 700 °C, probably due to high hydrogen
content. However, they exhibit high irreversible capacities, poor cycling stability, and
large voltage hysteresis with lithium intercalation happening just over 0 V and
deintercalation – around 1 V vs. $Li/Li^+$ [18]. Specific capacities decrease to 300 mAh/g or
lower if carbonisation temperatures exceed 1000 °C.

Hard carbons are increasingly becoming the material of choice for the negative
electrodes in lithium batteries. They demonstrate high capacities approaching 600 mAh/g
combined with good cycling stability and relatively small voltage hysteresis [16]. The
electronic conductivity of hard carbons (0.17 S/cm after carbonisation at 700 °C) [19] is
much lower than that of graphite (2x$10^3$ – 4x$10^3$ S/cm along graphene layers) [17].
However, these values are considered quite sufficient for using hard carbons as electrode
material in lithium-ion batteries [13]. Hard carbons are most often synthesised from a
variety of phenolic resins or from sugars. These precursors are cheap, readily available,
and, most importantly, can be easily infiltrated into the interstices of an opal template,
polymerised and carbonised there, yielding a 3D porous carbon matrix.

The carbon inverse opals used in this study were fabricated by polymerisation and
subsequent carbonisation from two sets of precursors: phenol-formaldehyde mixtures and
sucrose solutions as described in the following section.

7.2.2. **Preparation of silica-carbon composites**

7.2.2.1. **Phenolic route**

The first commercially available synthetic plastic called Bakelite was developed
in early 20th century by Dr. L.H. Baekeland and was, in fact, a phenol-formaldehyde
resin.

A hydroxymethyl phenol forms in the reaction between phenol and formaldehyde.
Phenol can react with formaldehyde at the ortho- and para- positions allowing in
principle up to three units of formaldehyde to be attached. This ratio is, however, never
achieved in practice. The hydroxymethyl group is capable of reacting with either another
phenol in its ortho- or para- site forming a methylene bridge, or with another
hydroxymethyl group forming an ether bridge. The properties of phenolic resin depend
greatly on the molar ratio of the reactants and on the choice of catalyst. In one particular
case of acid catalysis and phenol:formaldehyde ratio >1 a solid novolak resin is
obtained. Formation of possible isomers of Bisphenol F, the simplest novolak, is shown
in Equation 7.1 [20]:

```
Carbon inverse opals were synthesised from phenol-formaldehyde mixture via the acid catalysed route similarly to the methods described in the literature [7,8,15]. In detail, 10 parts by weight of phenol and 8 parts of 37 wt.% water solution of formaldehyde were mixed together giving a clear solution, then 1 part of catalyst (10 wt.% sulfuric acid) was added. The molar ratio of the components in the resulting solution was close to 1 : 0.84 : 0.09 (phenol : formaldehyde : sulfuric acid). Silica opal films were then immersed in the solution and kept there \textit{in vacuo} for 2 hours to ensure complete infiltration of the precursor into the interstices. After removal from the solution the top surface of the opal was gently pressed against a flat elastic polydimethylsiloxane (PDMS) sheet and fixed there with a foldback paper clip to ensure that no polymer overlayer would be formed. This ‘sandwich’ was then kept in air at 80 °C for 6 hours to evaporate most of the moisture, and for another 12 hours at 150 °C to get an \textit{in situ} cross-linked
polymer. After removal of the PDMS, the silica-polymer composite was carbonised at 800 °C for 12 hours under nitrogen atmosphere using a heating ramp of 2 °C/min.

7.2.2.2. Sucrose route

Sucrose has long been used for carbon production because of its availability and low cost. The chemical purity of table sugar leads to high reproducibility of the carbonisation process, and so it played an important role in early research of elemental carbon formation [21].

Sucrose is easily hydrolysed by dilute acids giving a mixture of D-glucose and D-fructose, commonly known as ‘inverse sugar’ [22].

![Equation 7.2](image)

On the other hand, concentrated and hot acids are well known to dehydrate sugars. Dehydration happens both by an intramolecular route leading to polyunsaturated conjugated structures like furfural, as well as by intermolecular condensation creating a well cross-linked polymer. This latter route is especially effective at high sugar concentrations [23].

Carbonisation of sucrose in the pores of silica opals was performed by a method adopted from references [2,3,6]. In detail, 35 g of sucrose were dissolved in 100 ml of water, and 1 ml of concentrated $H_2SO_4$ was added to the syrup leading to an ‘inverse sugar’ solution. The molar ratio of sucrose to sulphuric acid in the final mixture was 1 : 0.18. The solution was infiltrated into a silica opal for 2 hours in vacuo, and excess precursor was removed from top surface by PDMS sheet as described in the previous
section. Samples were then heated in air at 80 °C for 6 hours and for 12 hours at 150 °C. Heating caused slow evaporation of water inducing polycondensation of sugar catalysed by $H_2SO_4$. Infiltration and polymerisation steps were repeated up to 5 times to achieve higher carbon loading. The polymer-silica composite was heated under nitrogen atmosphere at a rate of 2 °C/min to 800-1000 °C and then pyrolysed at that temperature for 12 hours.

Both phenolic and sucrose methods produce silica-carbon composites as shown in Figure 7.3.

**7.2.2.3. Comparison of precursors**

Carbon content in the silica-carbon composites synthesised from phenol-formaldehyde and sucrose precursors was compared by energy-dispersive X-ray spectroscopy (EDX). For this purpose three silica colloidal crystal films were infiltrated once with the phenol-formaldehyde mixture (samples S250-CPF, S480-CPF and S890-CPF, where 250, 480 and 890 represent silica sphere diameter in nanometres) and three silica films of similar thickness with sucrose (samples S250-CSU, S480-CSU, S890-CSU). The films were carbonised at 800 °C as described in previous sections. Cross-sectional EDX analysis of the silica-carbon composites was then performed at six random spots of each sample to estimate carbon content. The results are summarised in Table 7.1.
Table 7.1.

Carbon content in silica-carbon composites synthesised from phenolic and sucrose precursors.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Sample name</th>
<th>Carbon content, at. %</th>
<th>Standard deviation σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol-Formaldehyde</td>
<td>S250-CPF</td>
<td>1.01</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>S480-CPF</td>
<td>2.55</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>S890-CPF</td>
<td>2.06</td>
<td>0.43</td>
</tr>
<tr>
<td>Sucrose</td>
<td>S250-CSU</td>
<td>10.08</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>S480-CSU</td>
<td>11.17</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>S890-CSU</td>
<td>7.30</td>
<td>2.32</td>
</tr>
</tbody>
</table>

Deviation of the carbon content values is quite high when different samples are compared, and even for different spots of the same sample. This is at least partially due to the limitations of the EDX spectroscopy method when applied to inhomogeneous samples with rough surface as was discussed in Section 4.2.3. Nevertheless, the data presented in Table 7.1 clearly indicates that the sucrose precursor produces composites with significantly higher carbon content.

It was also noticed during trials that carbonisation from sucrose precursor causes less cracking in the composite. This is probably due to a combination of two factors:

- a smaller degree of shrinking of the sugar precursor during pyrolysis comparing to phenol-formaldehyde;
- the thicker carbon walls in the case of sucrose that keep the silica particles in their place, not allowing them to sinter together at temperatures above silica softening point.
Due to these facts sucrose was chosen as a precursor for syntheses of inverse carbon opals, carbon-silicon composites and silicon-carbon composites (Chapter 8) that were used in electrochemical studies.

7.2.2.4. Influence of repetitive infiltrations on the carbon content

In order to increase the amount of carbon in the silica-carbon composite material and in the inverse opal, additional infiltrations can be performed after polymerisation. Unfortunately, infiltration fails if attempted after the carbonisation step (when most of the shrinkage of the carbonaceous material happens) as the material becomes too hydrophobic to be uniformly wetted by the water based sucrose solution. The influence of additional infiltrations was studied by EDX spectroscopy. Five successive infiltrations and polymerisations of sucrose were performed on the silica opal made of 890 nm spheres. EDX analysis of six random cross-sectional spots was done after each infiltration-polymerisation cycle. The results are presented in Table 7.2:

<table>
<thead>
<tr>
<th>Infiltration #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon content, at. %</td>
<td>7.54</td>
<td>10.29</td>
<td>10.77</td>
<td>11.07</td>
<td>10.36</td>
</tr>
<tr>
<td>Standard deviation $\sigma$</td>
<td>1.05</td>
<td>1.25</td>
<td>1.26</td>
<td>1.32</td>
<td>1.27</td>
</tr>
</tbody>
</table>

The data in Table 7.2 suggests that no significant amount of precursor can be added to the composite after only the second infiltration. Three sucrose infiltrations were performed for most of the carbon inverse opals used in this study, thus ensuring the highest carbon content achievable by the present method of synthesis.
7.2.3. *Silica template removal*

Silica spheres were removed by etching overnight with a 2% aqueous solution of hydrofluoric acid HF resulting in carbon inverse opal films. The main difference from the same process described in Section 6.2.3 is that unlike hydrogenated amorphous silicon glassy carbon does not react with dilute HF solutions and thus precise control of etching time is not required.

Properly performed fabrication of carbon inverse opals results in black iridescent films. Photographs of carbon inverse opals are presented in Figure 7.2.

![Figure 7.2](image)

Photographic depictions of carbon inverse opals.

7.3. **Characterisation of as-Synthesised Carbon Inverse Opals**

7.3.1. *SEM characterisation*

SEM images of the composite materials before removal of silica spheres are shown in Figure 7.3. Note that the carbon layer on the 480 nm silica spheres is thin and porous enough to look semitransparent at the accelerating voltage of 5 kV.
Figure 7.3.

Silica-carbon composites: (a) 480 nm spheres, (b) 890 nm spheres.

Carbon inverse opals are demonstrated in Figure 7.4. The materials possess ordered macroporosity and carbon is uniformly distributed throughout the opal thickness (Figure 7.4.a). The porous structure of the back side of the film (Figure 7.4.d) is a further indication that the porosity of the material is maintained all the way to the bottom. Higher magnification image (Figure 7.4.c) reveals the rough porous surface of carbon.
Figure 7.4.
Carbon inverse opals: (a) cross-sectional view of 15 μm thick film templated from 480 nm spheres, (b) low magnification top view of a film from 890 nm spheres, (c) high magnification view of inverse opal from 480 nm spheres, (d) low magnification view of a bottom side of inverse opal from 890 nm spheres.

7.3.2. μ-Raman

The structure of carbon inverse opals pyrolysed at 1000 °C was studied by Raman micro-spectroscopy as described in Section 4.2.5. A typical spectrum is presented in Figure 7.5. Two broad peaks are observed at 1350 cm\(^{-1}\) and at 1600 cm\(^{-1}\). The first, so-called D band peak characterises breakdown of symmetry at the edges of graphene sheets, and the G band at 1600 cm\(^{-1}\) arises from the E\(_{2g}\) vibrational mode of graphitic sp\(^2\)
carbon structures [24,25]. The G/D peak area ratio obtained for different samples varies from 0.52 to 0.57, which is similar to literature data for glassy carbons [9,26].

![Raman spectrum of carbon inverse opal carbonised at 1000 °C.](image)

**Figure 7.5.**

Raman spectrum of carbon inverse opal carbonised at 1000 °C.

### 7.3.3. XPS

Carbon inverse opal films templated from 890 nm spheres and pyrolysed at different temperatures were characterised by X-ray photoelectron spectroscopy. The elemental compositions of these materials calculated from XPS data are summarised in Table 7.3. and the corresponding C 1s spectra are presented in Figure 7.6:

**Table 7.3.**

Elemental composition of carbon inverse opal surfaces obtained by XPS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>800</td>
</tr>
<tr>
<td>C</td>
<td>83.65</td>
</tr>
<tr>
<td>O</td>
<td>16.12</td>
</tr>
<tr>
<td>F</td>
<td>0.23</td>
</tr>
</tbody>
</table>
Figure 7.6.

C 1s spectra of carbon inverse opals carbonised at different temperatures.

It is clear from Table 7.3 and Figure 7.6 that higher carbonisation temperatures lead to significant decreases in impurity content, and result in a narrower peak at 485 eV, smaller tail at higher binding energies and an overall ‘cleaner’ C 1s spectrum.

7.3.4. XRD

PXRD analysis of carbon inverse opals pyrolysed at 1000 °C was performed using the Siemens/Bruker AXS D5000 diffractometer within the range of 10° to 70° of 2θ. A typical pattern of amorphous material is presented in Figure 7.7. Only one very broad low intensity peak located between 15° and 30° can be definitely discerned.
7.3.5. **TGA**

Oxidative thermogravimetric analysis of inverse opals carbonised at 1000°C was performed in an air flow with the temperature increasing to 800 °C at a constant rate of 2 °C/min (Figure 7.8). The weight of the material gradually decreased due to loss of water and other absorbed volatile species until reaching 89.6 % of the original weight at 300 °C. Intense carbon oxidation started around 300 °C and continued until 650 °C. No non-volatile residue was left, indicating complete removal of the silica template by HF etching.
7.3.6. Conductivity measurements

Conductivities of materials templated from 890 nm spheres and carbonised at 800 °C, 900 °C and 1000 °C were measured by the two-probe method as described in Section 4.2.8. The values obtained are summarised in Table 7.4. There is a clear trend of conductivity improvement with the rise of carbonisation temperature. It is worth noting that the values obtained are significantly (an order of magnitude for material carbonised at 1000 °C) higher than the value reported by Yata et al. [19] for hard carbon synthesised by phenolic route at 700 C.

Table 7.4.

Conductivities of carbon inverse opals pyrolised at different temperatures.

<table>
<thead>
<tr>
<th>Carbonisation temperature, °C</th>
<th>Conductivity, S/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>0.68</td>
</tr>
<tr>
<td>900</td>
<td>1.48</td>
</tr>
<tr>
<td>1000</td>
<td>1.82</td>
</tr>
</tbody>
</table>
Electrochemical Performance of Carbon Inverse Opal Film Electrodes

7.4.1. Cyclic Voltammetry

Cyclic voltammetric plots of 15 μm thick carbon inverse opal films templated from 890 nm sphere opals are shown in Figure 7.9. The cells were cycled between 1.5 V and 50 mV vs. Li/Li⁺ at the scan rate of 0.1 mV/sec.
Figure 7.9.

CV curves of carbon inverse opal electrodes synthesised at different temperatures. Templating sphere size – 890 nm. Film thickness – ~15 μm. Scan rate – 0.1 mV/sec; scan range – 0.05-1.5 V vs. Li/Li⁺. Inverse opals were carbonised at: (a) 800 ºC; (b) 900 ºC; (c) 1000 ºC.

No well-pronounced peaks can be observed on the CV curves, instead, significant currents are passed at all voltages. Current increases gradually with decreasing voltage during the lithiation process, and then it slowly decreases during de-lithiation. Only very
small peaks around 0.12 V, 0.5 V and 1 V are present during the anodic process. Such behaviour can be explained by the fact that carbonaceous material is highly disordered and hence able to intercalate lithium over a wide range of potentials. In agreement with this, materials treated at higher temperatures tend to intercalate and de-intercalate more lithium at lower voltages as can be seen from Figure 7.9 and Table 7.5.
Table 7.5.
Charge transferred (expressed in percent of total charge transfer during half-cycle) at different voltages depending on the carbonisation temperature.

<table>
<thead>
<tr>
<th>Carbonisation Temperature, ºC</th>
<th>Cycle #</th>
<th>Lithiation</th>
<th></th>
<th></th>
<th>De-lithiation</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Charge transferred between 1.5 V and 1 V, %</td>
<td>Charge transferred between 1.5 V and 0.5 V, %</td>
<td>Charge transferred between 0.05 V and 0.5 V, %</td>
<td>Charge transferred between 0.05 V and 1 V, %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>1</td>
<td>17.7*</td>
<td>42.6</td>
<td>25.6</td>
<td>60.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.1</td>
<td>38.4</td>
<td>31.6</td>
<td>65.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>9.9</td>
<td>38.7</td>
<td>34.0</td>
<td>67.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>10.2</td>
<td>39.5</td>
<td>35.4</td>
<td>68.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>10.3</td>
<td>39.9</td>
<td>36.2</td>
<td>69.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>1</td>
<td>13.5*</td>
<td>38.3</td>
<td>39.5</td>
<td>73.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>7.8</td>
<td>34.9</td>
<td>43.4</td>
<td>75.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>7.7</td>
<td>34.9</td>
<td>44.2</td>
<td>76.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>7.9</td>
<td>35.7</td>
<td>45.9</td>
<td>77.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>8.0</td>
<td>36.0</td>
<td>46.5</td>
<td>77.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>1</td>
<td>11.3*</td>
<td>35.4</td>
<td>48.4</td>
<td>81.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>6.3</td>
<td>32.4</td>
<td>50.2</td>
<td>81.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>6.3</td>
<td>32.6</td>
<td>51.1</td>
<td>82.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>6.4</td>
<td>33.1</td>
<td>52.0</td>
<td>82.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>6.5</td>
<td>33.5</td>
<td>52.4</td>
<td>82.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Charge transferred between OCV voltage and 1 V, %

7.4.2. **Galvanostatic cycling**

The cycling behaviour of carbon inverse opal electrodes prepared from opals of different sphere sizes and heat-treated at different temperatures was studied by
galvanostatic cycling of coin cells described in Section 4.3.3 between 0.05 V and 2 V vs. Li/Li$^+$ at current rates ranging from C/10 to 10C. The same sequence of current rates as for silicon electrodes was used (see Table 6.7). C rates were calculated based on the theoretical capacity of graphite – 372 mAh/g, corresponding to the LiC$_6$ composition. Figure 7.10 demonstrates cycling performance of 15 μm thick inverse opal films prepared from 890 nm spheres and carbonised at 800 °C, 900 °C and 1000 °C. The cycling behaviour of 10 μm electrodes synthesised using 250 nm, 480 nm and 890 nm spheres and carbonised at 1000 °C is presented in Figure 7.11.
Figure 7.10.

Galvanostatic cycling of 15 μm thick carbon inverse opal electrodes templated from 890 nm spheres:
cycling behaviour (a) and charge transferred – voltage curves for selected cycles (b) of film carbonised at 800 ºC; cycling behaviour (c) and charge transferred – voltage curves (d) of film carbonised at 900 ºC; cycling behaviour (e) and charge transferred – voltage curves (f) of film carbonised at 1000 ºC.
Figure 7.11.

Galvanostatic cycling of 10 μm thick carbon inverse opal electrodes carbonised at 1000 ºC. Materials are templated from: (a) 250 nm spheres; (b) 480 nm spheres; (c) 890 nm spheres.

Electrodes demonstrate de-lithiation capacities in the range of 220-350 mAh/g, which is comparable to the inverse carbon opal electrodes previously reported in the literature [9,10], and excellent cycling performance with virtually no decrease in capacity.
during cycling. No apparent dependence of capacity values on carbonisation temperature or sphere size can be observed. However, electrodes treated at lower temperatures demonstrate significantly higher initial irreversible capacities, with the coulombic efficiency of electrode synthesised at 800 C being only 26.6 % during cycle 1, and these low efficiencies persist for larger number of cycles. The cycling performance of electrodes at C/10 rate is summarised in Table 7.6.

Table 7.6.
Cyclic performance of carbon inverse opals: capacities and coulombic efficiencies at cycles 1, 25 and 145.

<table>
<thead>
<tr>
<th>Cycle #</th>
<th>Sphere size, nm</th>
<th>890</th>
<th>890</th>
<th>480</th>
<th>250</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbonisation temperature, ºC</td>
<td>800</td>
<td>900</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>Film thickness, µm</td>
<td>15</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>De-lithiation capacity, mAh/g</td>
<td>284.3</td>
<td>249.0</td>
<td>273.0</td>
<td>215.5</td>
</tr>
<tr>
<td></td>
<td>Coulombic efficiency, %</td>
<td>26.6</td>
<td>51.5</td>
<td>61.1</td>
<td>56.1</td>
</tr>
<tr>
<td>25</td>
<td>De-lithiation capacity, mAh/g</td>
<td>311.2</td>
<td>262.3</td>
<td>284.2</td>
<td>223.7</td>
</tr>
<tr>
<td></td>
<td>Coulombic efficiency, %</td>
<td>98.3</td>
<td>99.5</td>
<td>99.4</td>
<td>99.5</td>
</tr>
<tr>
<td>145</td>
<td>De-lithiation capacity, mAh/g</td>
<td>314.9</td>
<td>260.5</td>
<td>283.1</td>
<td>222.4</td>
</tr>
<tr>
<td></td>
<td>Coulombic efficiency, %</td>
<td>98.6</td>
<td>99.4</td>
<td>99.7</td>
<td>99.6</td>
</tr>
</tbody>
</table>

Carbon inverse electrodes show good performances at high current rates with the capacities at 10C rate being up to 30 % of the capacities at C/10 rate. Hysteresis between lithiation and de-lithiation half-cycles during slow cycling is smaller for electrodes pyrolysed at higher temperatures, but at the same time hysteresis for high temperature electrodes grows faster with the increase of cycling rate, so that at high currents the situation is reversed and low-temperature electrodes demonstrate lower hysteresis levels (see Figure 7.10). Interestingly, this seems to have a small, if any, effect on the rate
performance of electrodes. No correlation between rate performance and either treatment temperature or sphere size has been observed. The rate performance data is summarised in Table 7.7 and Figure 7.12.

Table 7.7.
Rate performance of carbon inverse opal electrodes: de-lithiation capacities and coulombic efficiencies at different current rates.

<table>
<thead>
<tr>
<th>Cycle #</th>
<th>C rate</th>
<th>Sphere size, nm</th>
<th>890</th>
<th>900</th>
<th>1000</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Carbonisation temperature, °C</td>
<td>800</td>
<td>900</td>
<td>1000</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Film thickness, μm</td>
<td>15</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>C/10</td>
<td>De-lithiation capacity, mAh/g</td>
<td>312.0</td>
<td>262.0</td>
<td>284.2</td>
<td>223.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>98.3</td>
<td>99.3</td>
<td>99.5</td>
<td>99.6</td>
</tr>
<tr>
<td>30</td>
<td>C/5</td>
<td>De-lithiation capacity, mAh/g</td>
<td>279.2</td>
<td>234.6</td>
<td>253.4</td>
<td>186.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>99.3</td>
<td>99.5</td>
<td>99.6</td>
<td>99.5</td>
</tr>
<tr>
<td>50</td>
<td>C/2</td>
<td>De-lithiation capacity, mAh/g</td>
<td>227.1</td>
<td>196.1</td>
<td>205.7</td>
<td>145.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>99.4</td>
<td>99.3</td>
<td>99.7</td>
<td>99.5</td>
</tr>
<tr>
<td>70</td>
<td>1C</td>
<td>De-lithiation capacity, mAh/g</td>
<td>184.0</td>
<td>165.6</td>
<td>179.7</td>
<td>118.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>97.7</td>
<td>99.3</td>
<td>99.8</td>
<td>98.9</td>
</tr>
<tr>
<td>90</td>
<td>2C</td>
<td>De-lithiation capacity, mAh/g</td>
<td>138.2</td>
<td>141.2</td>
<td>144.5</td>
<td>78.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>99.0</td>
<td>99.3</td>
<td>99.2</td>
<td>99.1</td>
</tr>
<tr>
<td>110</td>
<td>5C</td>
<td>De-lithiation capacity, mAh/g</td>
<td>96.6</td>
<td>104.2</td>
<td>100.8</td>
<td>38.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>100.2</td>
<td>97.5</td>
<td>99.3</td>
<td>102.4</td>
</tr>
<tr>
<td>130</td>
<td>10C</td>
<td>De-lithiation capacity, mAh/g</td>
<td>10.4</td>
<td>74.0</td>
<td>67.2</td>
<td>13.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>123.9</td>
<td>101.8</td>
<td>99.3</td>
<td>103.6</td>
</tr>
</tbody>
</table>
7.4.3. Physical characterisation of cycled material

7.4.3.1. SEM characterisation

The sample preparation of carbon inverse opals after cycling and their transfer into the SEM apparatus was performed as described in Section 4.2.2 to avoid reaction of lithiated material with air. No morphological changes of the material can be observed even after 145 galvanostatic cycles (Figure 7.13). Some structural damage apparent from the SEM images is probably caused by mechanical pressure inside the coin cell and not by cycling.
Changes in material morphology at different lithiation stages were also studied by SEM. Inverse opals templated from 890 nm spheres and carbonised at 1000 °C were cycled galvanostatically at C/10 rate in the range between 2 V and 50 mV for twenty cycles. Cycling was stopped during the lithiation process of cycle 21 at 2 V (at the end of the 20th cycle), 300 mV and 50 mV (end of lithiation half-cycle). Amounts of lithium intercalated at these stages are summarised in Table 7.8. SEM images of electrodes at different degrees of lithiation are shown in Figure 7.14. The walls of lithiated electrodes look slightly thicker; however, the difference is not significant and should not affect the macroporosity of the material.
Table 7.8.
Composition of electrode materials at different degrees of lithiation used for SEM imaging.

<table>
<thead>
<tr>
<th>Voltage, V</th>
<th>Charge transferred in comparison with charge at full lithiation in cycle 20, %</th>
<th>x in Li$_x$C$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.30</td>
<td>53.2</td>
<td>0.41</td>
</tr>
<tr>
<td>0.05</td>
<td>100.0</td>
<td>0.73</td>
</tr>
</tbody>
</table>
Figure 7.14.

Carbon inverse opal electrodes (890 nm spheres, 15 μm thick, carbonised at 1000 °C) at different degrees of lithiation: (a) de-lithiated; (b) $Li_{0.41}C_6$; (c) $Li_{0.73}C_6$. 
7.4.3.2. \textbf{\( \mu \)-Raman}

Carbon inverse opals after electrochemical cycling were characterised by Raman micro-spectroscopy. Electrodes used for \( \mu \)-Raman spectroscopy were protected from atmosphere as described in Section 4.2.5. A typical spectrum of the electrode material carbonised at 1000 °C after 145 galvanostatic cycles is presented in Figure 7.15. The D band has a maximum at 1345 cm\(^{-1}\) and G band at 1580 cm\(^{-1}\). The G/D peak area ratios for different samples vary from 0.54 to 0.59. Overall, Raman spectra of carbon inverse opals after cycling do not differ significantly from the spectra of pristine materials.

![Figure 7.15.](image)

Raman spectrum of carbon inverse opal after galvanostatic cycling.

7.5. \textbf{Conclusions}

Inverse opal films of hard non-graphitisable carbon were synthesised by liquid phase infiltration, thermal polymerisation and pyrolysis from two precursors: phenol-formaldehyde mixture and sucrose. Sucrose was chosen for further syntheses as it provides higher carbon content in the product compared to a phenolic resin precursor. The optimal number of subsequent infiltration-polymerisation cycles was found to be three. Influence of the carbonisation temperature on chemical composition and electrical
properties of carbon structures was also studied. Characterisation of carbon inverse opals was performed by a variety of analytical techniques such as SEM combined with EDX spectroscopy, μ-Raman spectroscopy, XPS, XRD, TGA and two-probe conductivity measurements.

Electrochemical performance of carbon inverse opals was studied by both cyclic voltammetry and multiple cycling in the galvanostatic regime. Materials demonstrated excellent cycling stability and high rate capabilities. Interestingly, no correlation between template sphere size or carbonisation temperature and cycling performance has been observed. Cycled electrodes were characterised by SEM and μ-Raman spectroscopy.

7.6. References


CHAPTER 8.

SYNTHESIS AND ELECTROCHEMICAL CHARACTERISATION OF SILICON-CARBON AND CARBON-SILICON COMPOSITE INVERSE OPAL MATERIALS

8.1. Preamble

The possibility of introducing a second, third, etc. ingredient into an opal and especially into an inverse opal provides researchers with unique opportunities of creating new composite materials with periodic 3D structures. These materials can retain their macroporosity, allowing, for example, to make advantageous use of the properties of thin film materials combined with the high surface area of inverse opals; or the pores can be fully infiltrated producing unique interpenetrating materials. Such composite materials have been synthesised by several research groups, and their potential use as catalysts, sensors, fuel cell and battery materials has been demonstrated.

In this chapter I present a detailed description of synthetic procedures used for the fabrication of carbon-silicon composite inverse opal films. Two different approaches for making such composites were used:

- In the first approach inverse silicon opals synthesised by CVD were infiltrated with sucrose solution and pyrolysed, producing a silicon structure covered with a thin film of carbon (Section 8.3.1).
The other approach includes the synthesis of carbon inverse opal films from sucrose and subsequent deposition of thin silicon layers via CVD in the interstices of the carbon inverse opals (Section 8.5.1).

These composites were characterised by SEM, μ-Raman spectroscopy, XPS, TGA and two probe conductivity measurements (Sections 8.3.2 and 8.5.2).

Electrochemical testing of the composite materials was performed in voltammetric (Sections 8.4.1 and 8.6.1) and galvanostatic (Sections 8.4.2 and 8.6.2) modes at a variety of current rates. Changes in the material structure caused by electrochemical cycling were studied by SEM and μ-Raman spectroscopy (Sections 8.4.3 and 8.6.3).

8.2. Literature Review of Macroporous Composites Based on Inverse Opal Structures

Fabrication of composite materials based on colloidal crystal structures has attracted the attention of several research groups in recent years due to the flexibility these materials provide in terms of tuning their porosity and chemical properties. Applications were suggested for inverse opal composites in such fields as sensing, catalysis, fuel cell and battery technology.

The interstices in inverse opals are large enough to immobilise biological molecules such as enzymes and proteins. These composite structures can then be used in biosensing, biocatalysis, or as biofuel cells. Ultra-microelectrodes, as well as cm\(^2\)-sized electrodes, made of electrodeposited gold inverse opals have been modified with a bioelectrocatalytical system containing a redox mediator, a NADH cofactor, and glucose.
dehydrogenase. These electrodes, when used for amperometric detection of glucose, provided up to two orders of magnitude signal increase compared to nonporous electrodes [1,2]. Xia et al. [3] reported the adsorption of haemoglobin on electrodeposited gold inverse opal electrodes with 88.1% of the gold’s surface being covered by the protein. Direct electron transfer between adsorbate and the electrode was possible, while haemoglobin retained its biological activity.

A new approach to making proton conducting membranes was suggested by Munakata et al. [4]. The surface of a silica inverse opal film was sulfonated by 1,3-propanesultone which led to enhancement in proton conductivity by a factor of 400 comparing to unmodified material. A proton-conducting gel polymer was incorporated in the inverse opal to form a composite membrane that exhibited high proton conductivity similar to that of Nafion.

Chen et al. demonstrated via the use of platinum-titania inverse opal composites that photodegradation efficiency can be amplified four fold compared to titania nanoparticles [5]. Platinum nanoclusters were photodeposited on the surface of an inverse titania opal, which for the first time allowed a synergistic optical and chemical enhancement of the catalytic process to be achieved.

Kanamura, Dokko and colleagues synthesised inverse opals of the ceramic lithium-ion conductors \(Li_{0.35}La_{0.55}TiO_3\) [6] and \(Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3\) [7] by a sol-gel process. These materials can be used as solid electrolytes in lithium-ion batteries. The interstices of the inverse opals were filled with either the active electrode material \(Li_4Ti_5O_{12}\) or \(LiMn_2O_4\) by infiltration of sol-gel precursors and subsequent calcination.
This approach is believed to improve contact between electrode and electrolyte in solid state lithium batteries.

Carbon inverse opals are particularly popular among researchers as a base for composite materials because of the ease and low cost of carbon synthesis, its chemical stability, and high electronic conductivity. These integrated materials have been proposed for use as catalysts [8-11], sensors [12], battery electrodes [11, 13-15], and even complete lithium battery cells [16, 17].

Inverse carbons have been used by several research groups as supports for Pt and Pt-Ru catalysts for methanol oxidation in direct methanol fuel cells [8-11]. Catalyst nanoparticles were synthesised by the borohydride reduction method [18]. Reports demonstrated significant improvement of catalytic activity compared to commercially available carbon black materials.

Carbon inverse opals have been hydrothermally coated with continuous films of titania nanoparticles from titanium(IV) bis(ammonium lactato) dihydroxyde (TAL) precursor [12]. Negatively charged carboxylic groups were first created on the carbon surface via oxidation with nitric acid, and then covered in a layer-by-layer fashion with several layers of positively charged poly(diallyldimethylammonium chloride) (PDDA) and negatively charged poly(4-styrenesulfonate sodium) (PSS). This extensive surface preparation was required to increase the uniformity of the TiO₂ coatings.

As discussed in previous chapters, carbonaceous materials are widely used in Li-ion batteries as negative electrodes, and as conductive and binding additives to anode and cathode materials. Carbon anodes are the industry standard in state-of-the-art commercial batteries due to their high electronic conductivity, relatively fast lithium intercalation-
deintercalation, high cycling stability, low price and other factors. However, the limited capacity of carbon towards lithium drives researchers to look for alternative anode materials. Most high capacity materials suffer from one or more of the following:

- low electronic conductivity
- slow lithium diffusion
- significant volume changes during cycling

Use of nanosized or nanostructured materials and the creation of conductive carbon-based matrices has become a common approach to overcome some of these problems. Fabrication of composites based on inverse carbon opals and other electroactive materials is one of the possible approaches to increase efficiency of battery electrodes [11,13-17]. Lithium diffusion lengths in such composites are reduced to nanometres or tens of nanometres and electronic conductivity is provided by a carbon matrix, improving the rate capability of the electrode, while inverse opal structures gives enough open space for the material to expand during lithium insertion, increasing cycling stability.

Yamada et al. [13] coated carbon inverse opals with up to 30 wt.% of vanadium pentoxide, a promising cathode material for lithium-ion cells. Inverse opals were infiltrated with vanadium(V) hydrosol and then dried at an elevated temperature; the deposition was repeated several times in order to increase vanadia content. While the material did exhibit high rate capability, the authors did not provide any data on the cycling stability of the material.

Carbon-tin dioxide composites were prepared by Stein and colleagues [14] and their electrochemical behaviour was investigated. Tin(II) sulphate was first deposited on
the surface of a carbon inverse opal from an acidic solution, and then converted to tin oxide by heat treatment in a nitrogen atmosphere. $SnO_2$ particles, 10-40 nm in diameter, uniformly covered the carbon surface. The composite material demonstrated initial capacities higher than bare inverse carbon opal, however, capacities decreased after several cycles, attributed to detachment of lithiated nanoparticles due to their volume swings. Su et al. [11] synthesised carbon-tin dioxide composites by a different method, namely by the microwave-assisted hydrolysis of $SnCl_4$. This approach resulted in 5 nm particles coating the surface of a graphitic carbon inverse opal. Samples containing 18.6 wt.% and 74.5 wt.% of tin oxide were prepared. Both of them demonstrated initial capacities higher than bare carbon inverse opals. The capacity of the latter sample dropped to only 25% of the initial value after 30 cycles, while the former sample demonstrated reasonable cycle stability retaining 90.5% of its initial capacity after 60 cycles.

An interesting approach to modifying the properties of carbon inverse opals was suggested by Stein and colleagues [15]. First, a mesoporous/macroporous silica inverse opal is synthesised by templating poly(methyl methacrylate) (PMMA) colloidal crystal with silicate/poly(oxyethylene) surfactant solution. Calcination removes the PMMA spheres and surfactant, leaving a hierarchically porous silica inverse opal. This silica structure is then employed as a hard template to prepare a carbon replica by gas-phase phenolic polymerisation, carbonisation, and silica removal by $HF$ etching. In a final step, N-doped graphite is deposited by CVD from acetonitrile precursor first into the mesopores of a non-graphitisable carbon biporous structure, and after filling the mesopores within the voids of the inverse opal. Varying the CVD time allowed for
control of the graphitic content in the composite, wall thickness, mesoporosity, macroporosity, mechanical strength of the material and its electronic conductivity. Addition of graphitic carbon lowered the capacity for lithium at low charge rates, but increased the capacity at high rates. It also reduced the formation of a solid-electrolyte interface layer, thus lowering irreversible capacity during the first cycle.

Yet another example of carbon inverse opal composites used for Li-ion battery materials also comes from the Stein group [16,17]. A three dimensional interpenetrating electrochemical cell with carbon inverse opal anode, polyphenylene oxide (PPO) electrolyte and vanadium oxide gel cathode was fabricated and its operability demonstrated. The carbon inverse opal was first synthesised by a phenolic route then the PPO film was deposited under potentiostatic conditions. This composite was then soaked in LiClO$_4$ solution to introduce lithium ions to the polymer. The PPO-coated carbon anode was repeatedly filled under vacuum with tri-isopropoxide vanadium(V) oxide as the precursor material for the cathode, and then the carbon electrode was electrochemically lithiated using lithium foil. The capacity of the cell dropped sharply after several cycles, but nevertheless this demonstrated the feasibility of such an approach to battery design. Optimisation of such a system through improved electrode materials and synthetic procedures has the potential to drastically improve cell performance.
8.3. Fabrication and Characterisation of Silicon-Carbon Composite Inverse Opals

8.3.1. Synthesis of silicon-carbon composite inverse opal films

Fabrication of silicon-carbon composite materials was performed by infiltration of silicon inverse opals (Section 6.2) with a sucrose solution, followed by pyrolytic carbonisation (Section 7.2.2.2). The synthesis procedure is shown schematically in Figure 8.1.

Figure 8.1.

General procedure for fabrication of silicon-carbon composite inverse opals included the following steps: (1) formation of silicon inverse opal (see Section 6.2), (2) infiltration of silicon inverse opal with sucrose solution and pyrolysis.

In brief, the interstices of mechanically stabilised silica opals (Chapter 5) were infiltrated with amorphous silicon, and the silica template was removed by etching with 2% HF. Silicon inverse opals were then infiltrated with sucrose solution, carbon precursor was polymerised and pyrolysed for 12 hours in nitrogen at 800 °C. This procedure resulted in inverse opals composed of crystalline silicon coated with thin carbonaceous films. Unfortunately, uniform continuous coatings were never obtained, probably due to the hydrophobic nature of the silicon surface which prevented complete infiltration of sucrose solutions and/or caused formation of islands of polymer, rather than continuous films, during the drying and polymerisation steps.
8.3.2. Characterisation of silicon-carbon composite inverse opals

8.3.2.1. SEM

SEM images of the composites synthesised by the procedure described above are shown in Figure 8.2. Initial polymerisation of sucrose leads to a non-conductive coating that at least partially covers silicon surface (Figure 8.2.a-b) After pyrolysis the materials had ‘grainy’ structure and looked very similar to the crystallised silicon inverse opals (Figure 8.2.c-d). Carbon coating could not be observed in most cases after pyrolysis.

Figure 8.2.

Silicon-carbon composite inverse opals: (a)-(b) after sucrose infiltration and initial polymerisation, (c)-(d) after carbonisation at 800 °C.
8.3.2.2. \( \mu \)-Raman

The silicon and carbon-related Raman spectra taken at two randomly chosen spots of the same silicon-carbon composite inverse opal are shown in Figure 8.3. Peak positions, widths and intensities (normalised to silicon peaks) are summarised in Table 8.1. Narrow peaks at 521 cm\(^{-1}\) confirmed full conversion of silicon to the crystalline form. The shapes of the carbon-related peaks are similar to the carbon inverse opals (Section 7.3.2) suggesting formation of glassy carbon. Strong variations in carbon peak intensities indicate inhomogeneity of the carbon coating.

![Raman spectra](image)

**Figure 8.3.**

Raman spectra for two spots of silicon-carbon composite inverse opal synthesised from 890 nm spheres: (a) silicon peak, (b) carbon peaks.
Table 8.1.
Raman peak positions, full widths at half maximum, normalised to silicon peak intensities and $C_G/C_D$ area ratio for two spots of silicon-carbon composite inverse opal film synthesised from 890 nm spheres.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th></th>
<th>C_D</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position, cm$^{-1}$</td>
<td>FWHM, cm$^{-1}$</td>
<td>Position, cm$^{-1}$</td>
<td>Intensity</td>
<td>Position, cm$^{-1}$</td>
<td>Intensity</td>
<td>$C_G/C_D$ area ratio</td>
</tr>
<tr>
<td>Spot 1</td>
<td>521</td>
<td>7.5</td>
<td>1345</td>
<td>0.038</td>
<td>1600</td>
<td>0.089</td>
<td>0.62</td>
</tr>
<tr>
<td>Spot 2</td>
<td>521</td>
<td>7.2</td>
<td>1345</td>
<td>0.041</td>
<td>1600</td>
<td>0.094</td>
<td>0.60</td>
</tr>
</tbody>
</table>

8.3.2.3. **XPS**

The surface elemental composition of silicon-carbon composite inverse opals obtained by X-ray photoelectron spectroscopy is shown in Table 8.2 and the spectra of individual elements are demonstrated in Figure 8.4. Significant amounts of silicon suggest that the carbon coating was relatively thin, on the order of nanometres or few tens of nanometres at most. The shapes of $C\,1s$ and $Si\,2p$ peaks are very similar to the $C\,1s$ peaks of carbon inverse opals (Section 7.3.3) and to the $Si\,2p$ peak of crystalline silicon inverse opal (Section 6.2.6.3) respectively.

Table 8.2.
Elemental composition of silicon-carbon composite inverse opal surface obtained by XPS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Content, at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>42.4</td>
</tr>
<tr>
<td>Si</td>
<td>39.6</td>
</tr>
<tr>
<td>F</td>
<td>0.1</td>
</tr>
<tr>
<td>O</td>
<td>18.0</td>
</tr>
</tbody>
</table>
8.3.2.4. Conductivity

The conductivities of silicon-carbon composite inverse opals measured by a two-probe method varied widely from 4 mS/cm to 90 mS/cm. Such discrepancies between samples are probably caused by large variations in the continuity of the carbon coatings and, possibly, in their thicknesses.
8.4. Electrochemical Performance of Silicon-Carbon Composite

Inverse Opal Film Electrodes

8.4.1. Cyclic Voltammetry

Cyclic voltammetry of 10 μm thick silicon-carbon composite electrode templated from 890 nm silica spheres was performed between 1.5 V and 50 mV vs. Li/Li$^+$ at 0.1 mV/sec scan rate. The cyclic voltammetry plot is presented in Figure 8.5, peak positions and relative intensities are summarised in Table 8.3.

Significant lithiation offset around 0.35 V, and de-lithiation was mostly completed at 0.7 V. Two well-defined peaks are observed during the cathodic half-cycle – the first peak has an extremum at 0.2 V and the second peak does not reach its maximum before the reversion of the process direction. A small ‘bump’ is also observed around 0.26-0.29 V. Lithiation half-cycles during the first and to a lesser extent the second cycles differed from cycles 3-5 with the low voltage peak being much more strongly pronounced in comparison with the peak located at 0.2 V. Three anodic peaks located at 0.33 V, 0.43 V and 0.47-0.48 V were present during the first and second cycles. The relative intensity of the peak at 0.43 decreases from cycle 1 to cycle 2 and the peak disappeared by the third cycle.

The signal intensity decreases sharply with cycling as can be seen from Figures 8.5-8.6 and from Table 8.4. Overall, the shapes of silicon-carbon composite voltammograms strikingly resemble the CVs of crystalline silicon electrodes discussed in Section 6.3.2.1.
Figure 8.5.

CV curve of silicon-carbon composite inverse opal electrode. Silica template sphere size 890 nm. Film thickness – ~10 μm. Scan rate – 0.1 mV/sec; scan range – 0.05-1.5 V vs. Li/Li⁺.

Table 8.3.

Peak positions and relative intensities for cyclic voltammogram presented in Figure 8.5.

<table>
<thead>
<tr>
<th>Cycle #</th>
<th>Cathodic peak</th>
<th>Anodic peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak position, V</td>
<td>Relative intensity of value at 0.05 V to peak value</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>11.36*</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>2.49</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>1.53</td>
</tr>
<tr>
<td>4</td>
<td>0.20</td>
<td>1.57</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>1.58</td>
</tr>
</tbody>
</table>

* Relative intensity of value at 0.05 V to value at 0.20 V.
Table 8.4.
Change in the first anodic peak intensities with the cycle number.

<table>
<thead>
<tr>
<th>Cycle #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak intensity, mAh/g</td>
<td>1109</td>
<td>887</td>
<td>727</td>
<td>502</td>
<td>312</td>
</tr>
</tbody>
</table>

Figure 8.6.
Change in the first anodic peak intensities with the cycle number.

8.4.2. **Galvanostatic cycling**

Electrochemical performance of silicon-carbon composite inverse opal film electrodes prepared from 10 μm thick 890 nm silica opals was studied by galvanostatic cycling at C/10, 1C and 10C rates. Since the exact silicon to carbon ratio of the material is not known, calculations of C rates were based on the theoretical capacity of 3579 mAh/g corresponding to $Li_{15}Si_4$, as if the electrode material was composed of silicon only. Cycling performance of silicon-carbon composite inverse opals is presented in Figure 8.7.

Similarly to crystalline silicon inverse opals (Section 6.3.2.2), silicon-carbon composite inverse opal electrodes demonstrated high capacities during the first several
cycles, even at 10C rate, and fast degradation with the complete loss of capacity after 8-11 cycles.

Figure 8.7.

Galvanostatic cycling of 10 µm silicon-carbon composite inverse opal electrodes templated from 890 nm spheres: (a) cycling at C/10 rate; (b) cycling at 1C rate; (c) cycling at 10C rate.
8.4.3. **Physical characterisation of cycled material**

8.4.3.1. **SEM characterisation**

SEM images of silicon-carbon composites after galvanostatic cycling at C/10 rate are presented in Figure 8.8. Again, as in the case of cycled crystalline silicon (Section 6.3.2.3) the material appeared to have completely disintegrated and no macroporous structure is observed.

![SEM images of silicon-carbon composites after galvanostatic cycling at C/10 rate.](image)

Figure 8.8.

Silicon-carbon composites after 20 galvanostatic cycles at C/10 rate.

8.5. **Fabrication and Characterisation of Carbon-Silicon Macroporous Composite Inverse Opals**

8.5.1. **Synthesis of carbon-silicon composite inverse opal films**

Carbon-silicon composite films based on carbon inverse opal structures were fabricated from silica opals (Chapter 5) by a combination of sucrose carbonisation described in detail in Section 7.2.2.2, and dynamic silicon CVD, described in Section 6.2.1.4 of this thesis. The synthesis procedure is schematically depicted in Figure 8.9.
General procedure for fabrication of carbon-silicon inverse opal composites includes the following steps:

1. formation of carbon inverse opal (see Section 7.2),
2. silicon deposition by CVD from disilane.

Briefly, silica colloidal crystal films, mechanically stabilised by silica layer-by-layer deposition (Section 5.4) were infiltrated three times with a sucrose solution and were pyrolysed in nitrogen at 1000 °C. The silica template was etched away with 2% hydrofluoric acid. The obtained carbon inverse opals were coated with silicon by means of CVD from disilane. Silicon deposition times varied from 15 min to 90 min, producing approximately 20 nm to 100 nm thick uniform coatings. The thicknesses of the silicon films were estimated from SEM images. Materials having 50-70 nm thick walls (silicon CVD performed for 45 min) were used for electrochemical testing.

8.5.2. **Characterisation of carbon-silicon composite inverse opals**

8.5.2.1. **SEM**

SEM images of carbon-silicon composite inverse opal films templated from various sphere sizes are presented in Figure 8.10. Silicon deposition in all the cases in Figure 8.10 was performed for 45 minutes and resulted in 50-70 nm thick walls. All the structures remained macroporous, although the pore size is significantly diminished for the 250 nm sphere opal.
Figure 8.10.
Carbon-silicon composite inverse opals: (a),(b) templated from 250 nm spheres, (c),(d) templated from 480 nm spheres, (e),(f) templated from 890 nm spheres.
8.5.2.2. μ-Raman

Raman spectroscopy confirmed formation of an amorphous silicon coating on carbon inverse opals. A broad (FWHM 21.2 cm$^{-1}$) silicon peak is located at 481 cm$^{-1}$ and very weak carbon peaks are observed at 1344 cm$^{-1}$ and 1579 cm$^{-1}$. The low intensity of the carbon Raman bands can be explained by the presence of silicon coating that is weakening the carbon signal.

![Raman spectra for carbon-silicon composite inverse opal](image)

**Figure 8.11.**

Raman spectra for carbon-silicon composite inverse opal (templated from 890 nm spheres, silicon CVD 45 min): (a) silicon peak, (b) carbon peaks. Intensities are normalised to silicon peak.

8.5.2.3. XPS

The results of XPS analysis of carbon-silicon composite inverse opals synthesised by 45 min silicon CVD are shown in Table 8.5 and Figure 8.12. The elemental composition of the material is similar to the composition of the native oxide on the silicon surface [19]. It is also comparable to the results obtained for amorphous silicon inverse opals (Section 6.2.4.3) with the exception of negligible fluorine content in the former case, as the silicon-carbon composite had not been exposed to HF solutions or CHF$_3$ plasma after silicon deposition. Peak shapes are also very similar to the peaks of...
amorphous silicon. The carbon core of the composite material is shielded by a silicon layer and therefore cannot be probed by XPS.

Table 8.5.
Elemental composition of carbon-silicon composite inverse opal surface obtained by XPS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Content, at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>40.8</td>
</tr>
<tr>
<td>C</td>
<td>28.0</td>
</tr>
<tr>
<td>O</td>
<td>31.1</td>
</tr>
<tr>
<td>F</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Figure 8.12.

XPS spectra of carbon-silicon composite inverse opal material: (a) Si 2p, (b) C 1s, (c) O 1s.

8.5.2.4. TGA

Thermogravimetric analysis of carbon-silicon composite inverse opals was performed by the same procedure as the TGA of silicon inverse opals. Namely, a finely ground material was heated from room temperature to 1400 °C at the rate of 2 °C/min in air to achieve complete oxidation of carbon and silicon.
The TGA curve of the carbon-silicon composite inverse opal material templated from 890 nm spheres with silicon deposition time of 45 min is presented in Figure 8.13. The low temperature weight loss of 1.3 wt.% was caused by evaporation of water and other adsorbed impurities. Noticeable oxidation of carbon indicated by the weight loss started around 350 °C. The weight started to increase at 575 °C due to the oxidation of silicon and came to a plateau around 1200 °C. Silicon oxidation took place in two steps, closely resembling the TGA profile of amorphous silicon discussed in Section 6.2.4.4.

![TGA profile of carbon-silicon composite inverse opal.](image)

The TGA data was used to calculate the elemental composition of the materials. Two assumptions were made in order to allow for such calculations. Firstly, it was assumed that the initial material contains only silicon, carbon and oxygen. Secondly, the temperature profiles of carbon and silicon oxidation were considered to be identical to the profiles of carbon and silicon inverse opals obtained by TGA (Sections 7.3.5 and 6.2.4.4 respectively). The following equations can be then written:

\[ x_{Si} + x_O + x_C = 100 \% \]  

\textbf{Eq. 8.1,}
\[
\frac{x_{Si} + x_{O} + x_{C}}{x_{Si} + x_{O} + x_{add}^{650}} = \frac{m_{300}}{m_{650}}
\]

Eq. 8.2,

\[
\frac{x_{Si} + x_{O} + x_{add}^{650}}{x_{Si} + x_{O} + x_{add}^{650} + x_{add}^{1300}} = \frac{m_{650}}{m_{1300}}
\]

Eq. 8.3,

\[
\frac{x_{Si}}{x_{O} + x_{add}^{650} + x_{add}^{1300}} = \frac{M_{Si}}{2M_{O}}
\]

Eq. 8.4,

\[
\frac{x_{Si} + x_{O} + x_{add}^{650}}{x_{Si} + x_{O}} = 1.079
\]

Eq. 8.5,

where \(x_{Si}\), \(x_{O}\) and \(x_{C}\) are the weight fractions of silicon, oxygen and carbon in the material at 300 °C, \(x_{add}^{650}\) is the weight fraction of oxygen added during silicon oxidation from 300 °C to 650 °C, \(x_{add}^{1300}\) is the increase of weight fraction from 650 °C to 1300 °C, \(m_{300}\), \(m_{650}\) and \(m_{1300}\) are weights at indicated temperatures, \(M_{Si}\) and \(M_{O}\) are the atomic weights of silicon and oxygen. The number 1.079 in the right part of Equation 8.5 is found from the TGA curve of amorphous silicon inverse opal, where a 7.9 % increase in weight was observed between 300 °C and 650 °C.

The weight fractions of silicon, carbon and oxygen calculated in this manner for composites synthesised by 45 min silicon CVD from carbon inverse opals of different sphere sizes are summarised in Table 8.6. Interestingly, there is no correlation between sphere size and \(Si/C\) ratio. This suggests that the carbon inverse opals were indeed very porous and carbon occupied only small fraction of interstices between air spheres.
Table 8.6.
Elemental composition of carbon-silicon composite inverse opals obtained from TGA data.

<table>
<thead>
<tr>
<th>Sphere size, nm</th>
<th>Content, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>250</td>
</tr>
<tr>
<td>Si</td>
<td>86.3</td>
</tr>
<tr>
<td>C</td>
<td>8.2</td>
</tr>
<tr>
<td>O</td>
<td>5.5</td>
</tr>
</tbody>
</table>

8.5.2.5. Conductivity

Conductivity measurements of carbon-silicon composite inverse opal films were performed by two-probe method as discussed in Section 4.2.8. In brief, two co-planar aluminium electrodes were deposited via PVD onto the silicon surface of the composite, and currents were then measured at different bias voltages. The conductivities of the materials templated from 890 nm spheres and having silicon coatings of various thicknesses are shown in Table 8.7. As expected, conductivities decreased with the increase in silicon thickness. The conductivities of the silicon-carbon composite inverse opals were an order of magnitude lower than the conductivities of pristine carbon inverse opals (Section 7.3.6) and six orders of magnitude higher than the conductivities of amorphous silicon inverse opals (Section 6.2.4.6).

Table 8.7.
Conductivity of carbon-silicon composite inverse opals.

<table>
<thead>
<tr>
<th>Silicon CVD time, min</th>
<th>15</th>
<th>45</th>
<th>60</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wall thickness*, nm</td>
<td>20-25</td>
<td>50-70</td>
<td>70-85</td>
<td>110-140</td>
</tr>
<tr>
<td>Conductivity, S/cm</td>
<td>0.71</td>
<td>0.42</td>
<td>0.20</td>
<td>0.11</td>
</tr>
</tbody>
</table>

* Estimated from SEM images.
8.6. Electrochemical Performance of Carbon-Silicon Composite Inverse Opal Film Electrodes

8.6.1. Cyclic Voltammetry

Cyclic voltammetry of carbon-silicon composite inverse opal films templated from 10 μm thick silica opals composed of 250 nm, 480 nm and 890 nm spheres was performed in the range between 1.5 V and 0.05 V vs. Li/Li⁺ at 0.1 mV/sec scan rate. The CV curves are presented in Figure 8.14.
Figure 8.14.

CV curves of carbon-silicon macroporous composite inverse opal film electrodes. Film thickness ~10 μm.

Scan rate – 0.1 mV/sec; scan range – 0.05-1.5 V vs. Li/Li⁺. Materials are templated from 250 nm (a), 480 nm (b), and 890 nm (c) spheres.

Significant lithiation started at about 0.35 V, and de-lithiation was finished by 0.6-0.7 V. The positions and relative intensities of cathodic (lithiation) and anodic (de-lithiation) peaks are summarised in Table 8.8.
Table 8.8.

Peak positions and relative intensities for cyclic voltammograms presented in Figure 8.5.

| Sphere size, nm | Cycle | Cathodic peak | Anodic peaks | | | |
| | | Peak position, V | Relative intensity of value at 0.05 V to peak value | Peak positions, V | Relative intensity of peak 1 to peak 2 | | |
| | | | | 1 | 2 | | |
| 250 | 1 | - | 2.03* | 0.33 | 0.48 | 1.31 | |
| | 2 | 0.20 | 1.49 | 0.33 | 0.48 | 1.30 | |
| | 3 | 0.20 | 1.54 | 0.33 | 0.48 | 1.26 | |
| | 4 | 0.20 | 1.57 | 0.33 | 0.48 | 1.26 | |
| | 5 | 0.20 | 1.56 | 0.33 | 0.48 | 1.26 | |
| 480 | 1 | - | 1.86* | 0.36 | 0.48 | 1.20 | |
| | 2 | 0.20 | 1.51 | 0.33 | 0.48 | 1.30 | |
| | 3 | 0.20 | 1.53 | 0.33 | 0.48 | 1.26 | |
| | 4 | 0.20 | 1.56 | 0.33 | 0.48 | 1.25 | |
| | 5 | 0.20 | 1.56 | 0.33 | 0.48 | 1.26 | |
| 890 | 1 | - | 2.19* | 0.34 | 0.48 | 1.25 | |
| | 2 | 0.20 | 1.40 | 0.33 | 0.48 | 1.25 | |
| | 3 | 0.20 | 1.42 | 0.33 | 0.48 | 1.24 | |
| | 4 | 0.20 | 1.41 | 0.33 | 0.48 | 1.23 | |
| | 5 | 0.20 | 1.41 | 0.33 | 0.48 | 1.23 | |

* Relative intensity of value at 0.05 V to value at 0.20 V.

The CV curves are very similar to the case of amorphous silicon discussed in Section 6.3.1.1. As before, the first cycle is quite distinct from the following ones, especially during lithiation. From cycle 2 and beyond the curves have very similar shapes and intensities, suggesting a highly reversible reaction. In contrast to the case of silicon
inverse opals the position of the first anodic peak did not change with the sphere size, probably due to the fact that thicknesses of silicon layer and hence lithium diffusion lengths were similar for all the sphere sizes.

### 8.6.2. **Galvanostatic cycling**

The cycling behaviour of carbon-silicon composite inverse opal electrodes was studied by galvanostatic cycling between 0.05 V and 2 V vs. $\text{Li/Li}^+$ at current rates ranging from C/10 to 10C. The same sequence of current rates was used as for cycling of amorphous silicon inverse opal and carbon inverse opal electrodes (see Table 6.7 in Section 6.3.1.2). Similar to the silicon-carbon composites, C rates were calculated basing on the assumption that the material was composed of silicon only since the exact compositions of the materials were not known, and the TGA experiments confirmed that carbon content does not exceed 10 wt. % in the materials synthesised under similar conditions.

5 and 10 $\mu$m thick films templated from 250 nm spheres; 5, 10 and 15 $\mu$m thick films from 480 nm spheres; and 5, 10 and 15 $\mu$m thick films from 890 nm spheres were used for galvanostatic experiments. Cycling behaviour of these electrodes is shown in Figures 8.15-8.17 and some important characteristics are summarised in Table 8.9.
Galvanostatic cycling of carbon-silicon composite inverse opal film electrodes templated from 250 nm spheres: (a) Cycling behaviour of 5 μm film; (b) charge transferred – voltage curves for selected cycles of 5 μm film; (c) cycling behaviour of 10 μm film; (d) charge transferred – voltage curves for selected cycles of 10 μm film.
Figure 8.16.

Galvanostatic cycling of carbon-silicon composite inverse opal film electrodes templated from 480 nm spheres: (a) Cycling behaviour of 5 μm film; (b) charge transferred – voltage curves for selected cycles of 5 μm film; (c) cycling behaviour of 10 μm film; (d) charge transferred – voltage curves for selected cycles of 10 μm film; (e) cycling behaviour of 15 μm film; (f) charge transferred – voltage curves for selected cycles of 15 μm film.
Figure 8.17.
Galvanostatic cycling of carbon-silicon composite inverse opal film electrodes templated from 890 nm spheres: (a) Cycling behaviour of 5 μm film; (b) charge transferred – voltage curves for selected cycles of 5 μm film; (c) cycling behaviour of 10 μm film; (d) charge transferred – voltage curves for selected cycles of 10 μm film; (e) cycling behaviour of 15 μm film; (f) charge transferred – voltage curves for selected cycles of 15 μm film.
The carbon-silicon composite inverse opal electrodes demonstrated high delithiation capacities around 2000 mAh/g in the first cycle (Table 8.9). Coulombic efficiencies during the first cycle lie in the range of 70 to 80%. They increased with the increase of sphere diameter, but the trend was less pronounced than in the case of silicon inverse opal electrodes (Section 6.3.1.2). Carbon-silicon composite inverse opals probably had higher surface areas than silicon inverse opals due to increased surface roughness. On the other hand, unlike silicon inverse opals, composite materials were not treated with HF after silicon deposition, and so had less impurity on the silicon surface. These two factors should have opposite effects on the initial irreversible capacity of carbon-silicon electrodes, leading to somewhat lower efficiencies of composite inverse opals with large macropores in comparison with inverse silicon opals, and similar or even slightly higher efficiencies for materials with smaller pores. After 3-5 galvanostatic cycles coulombic efficiencies increased to 97-99%.

Carbon-silicon electrodes demonstrated very good cycling stability with capacity retention over 80% after 145 cycles for the majority of samples. Similar to silicon, inverse opal composite electrodes templated from larger spheres, cycle better. Interestingly, the difference in cycling stability was also less pronounced than in the silicon inverse opal electrodes. It seems that the carbon ‘backbone’ somehow prevented complete clogging of the pores by lithiated silicon.
Table 8.9.

Cyclic performance of carbon-silicon composite inverse opal film electrodes: initial capacities and coulombic efficiencies, capacity retentions and coulombic efficiencies after 25 and 145 galvanostatic cycles.

| Cycle # | Sphere size, nm | 250 |       | 480 |  |       | 890 |       |
|---------|----------------|-----|-------|-----| |       |     |-------|
|         | Film thickness, μm |     |       |     | |       |     |       |
| 1       | De-lithiation capacity, mAh/g | 2406 | 1890 | 1905 | 2557 | 1736 | 2165 | 2195 | 2374 |
|         | Coulombic efficiency, % | 71.2 | 67.3 | 75.5 | 76.5 | 75.7 | 78.1 | 79.5 | 77.5 |
| 25      | Capacity retention, % | 96.8 | 90.6 | 95.5 | 94.0 | 92.4 | 94.9 | 91.2 | 94.5 |
|         | Coulombic efficiency, % | 98.2 | 96.5 | 98.2 | 98.9 | 98.3 | 98.2 | 96.9 | 97.9 |
| 145     | Capacity retention, % | 88.6 | 56.2 | 82.7 | 86.9 | 72.4 | 87.6 | 84.1 | 91.0 |
|         | Coulombic efficiency, % | 97.6 | 95.6 | 98.2 | 98.8 | 98.4 | 98.2 | 96.8 | 97.8 |

Rate performance of carbon-silicon composite inverse opal electrodes is summarised in Table 8.10 and Figure 8.18. Capacities decreased exponentially with increasing current. Rate capabilities of composite electrodes were remarkably improved in comparison to silicon inverse opals. The capacities delivered at a 1C rate are 35-55 % of the capacities at a C/10 rate. The capacities of most electrodes decreased to negligible levels by the 10C rate. Rate performances do not correlate with electrode thicknesses. This suggests that, unlike inverse silicon opals, conductivity of the electrode material is not the rate-controlling step of the electrochemical reaction.
Table 8.10.
Rate performance of carbon-silicon composite inverse opal film electrodes: de-lithiation capacities and
coulombic efficiencies at different current rates.

<table>
<thead>
<tr>
<th>Cycle #</th>
<th>C rate</th>
<th>Sphere size, nm</th>
<th>250</th>
<th>480</th>
<th>890</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Film thickness, μm</td>
<td>5</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Capacity, mAh/g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>C/10</td>
<td>2334 1735 1831 2406 1625</td>
<td>2066 2012 2249</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>98.2 96.6 98.0 98.9 98.3</td>
<td>98.2 96.8 97.9</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>C/5</td>
<td>2008 1434 1525 1792 1269</td>
<td>1683 1630 1704</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>98.3 96.6 98.0 98.8 98.5</td>
<td>98.2 96.6 97.8</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>C/2</td>
<td>1497 998 1049 1464 970</td>
<td>1086 1133 1127</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>98.2 96.4 98.3 98.9 98.6</td>
<td>98.2 96.7 97.7</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>1C</td>
<td>1226 664 857 1097 606</td>
<td>771 870 741</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>97.9 96.3 98.3 98.8 98.5</td>
<td>97.8 95.8 97.4</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>2C</td>
<td>743 471 484 884 347</td>
<td>612 529 444</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>97.4 95.6 97.1 98.4 97.7</td>
<td>97.4 94.9 97.2</td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>5C</td>
<td>387 234 202 386 18</td>
<td>97 197 44</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>96.2 93.9 96.0 98.0 121</td>
<td>93.2 93.9 88.2</td>
<td></td>
</tr>
<tr>
<td>130</td>
<td>10C</td>
<td>81 16 16 62 12</td>
<td>18 12 16</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coulombic efficiency, %</td>
<td>92.3 103 96.1 96.9 125</td>
<td>64.9 107 32.0</td>
<td></td>
</tr>
</tbody>
</table>
8.6.3. **Physical characterisation of cycled material**

8.6.3.1. **SEM characterisation**

SEM imaging of galvanostatically cycled electrodes (Figure 8.19) showed that the macroporous structures remained largely intact and silicon coating was well-preserved on the carbon matrix.
Figure 8.19.

Carbon-silicon composite inverse opals after 145 galvanostatic cycles: (a),(b) materials templated from 250 nm spheres, (c),(d) materials templated from 480 nm spheres, (e),(f) materials templated from 890 nm spheres.

Morphology changes caused by lithiation were also visualised by SEM. Electrodes templated from 890 nm spheres were cycled at a C/10 rate in the range
between 2 V and 50 mV for twenty cycles. Cycling was then stopped either at 2 V after cycle 20, at 0.1 V during the lithiation process of cycle 21, or after cycle 21 on lithiation completion at 0.05 V. Table 8.11 summarises lithium content in the structures studied and Figure 8.20 presents SEM images of these structures. De-lithiated structures closely resembled pristine silicon inverse opals, indicating a high reversibility of electrochemical lithium insertion. Partially lithiated electrodes had thicker walls and smaller pores between the air spheres; the structures, however, remained highly open and accessible to electrolyte. Walls became increasingly thick with the increasing of lithium content, but structures remained macroporous even at the highest degree of lithiation.

Table 8.11.
Composition of electrode materials at different degrees of lithiation used for SEM imaging.

<table>
<thead>
<tr>
<th>Voltage, V</th>
<th>Charge transferred in comparison with charge at full lithiation in cycle 20, %</th>
<th>x in Li$_x$Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.10</td>
<td>44.2</td>
<td>1.02</td>
</tr>
<tr>
<td>0.05</td>
<td>99.9</td>
<td>1.87</td>
</tr>
</tbody>
</table>
Figure 8.20.

Amorphous silicon inverse opals at different degrees of lithiation: (a) delithiated silicon; (b) $Li_{1.02}Si$; (c) $Li_{1.87}Si$. 
8.6.3.2. **μ-Raman**

Raman spectra of carbon-silicon composite inverse opals after 145 cycles are shown in Figure 8.21. The broad (FWHM 19.8 cm\(^{-1}\)) silicon peak is shifted from 481 cm\(^{-1}\) to 486 cm\(^{-1}\). A similar, but larger shift was observed for cycled silicon inverse opals (Section 6.3.1.3), and is probably caused by mechanical stress induced during lithiation [20]. The B and G carbon bands have maxima at 1350 cm\(^{-1}\) and 1590 cm\(^{-1}\) respectively. Importantly, the carbon signal is still very weak, which indicates that silicon uniformly covers the carbon matrix even after extensive cycling.

![Figure 8.21.](image)

Raman spectra for carbon-silicon composite inverse opals (templated from 890 nm spheres, silicon CVD – 45 min): (a) silicon peak, (b) carbon peaks. Intensities are normalised to silicon peak.

**8.7. Conclusions**

Silicon-carbon composite inverse opals were fabricated by a multi-step process. Initially, a silica opal template was infiltrated with amorphous silicon by CVD; secondly, silica was selectively removed resulting in silicon inverse opal; and thirdly, a thin ‘patchy’ layer of carbon was introduced by infiltration and carbonisation of sucrose. An analogous approach was used to synthesise carbon-silicon composite inverse opals: silica
colloidal crystal was infiltrated with sugar that was then pyrolytically converted to hard carbon; the silica template was removed to produce a carbon inverse opal; and then carbon surface was coated by CVD with a thin uniform continuous silicon layer. These structures were characterised by a variety of analytical techniques including SEM, μ-Raman, XPS, TGA and conductivity measurements.

Electrochemical performance of composite inverse opal film electrodes was studied by cyclic voltammetry and by galvanostatic cycling. Cycled electrode materials were characterised by SEM and μ-Raman spectroscopy.

The electrochemical behaviour of silicon-carbon composite inverse opals was similar to crystalline silicon inverse opals. The material demonstrates excellent rate performance during initial cycles, but rapid capacity fading caused by the disintegration of the macroporous structure makes the use of these materials as lithium-ion battery anodes impractical. Carbon-silicon composite inverse opals demonstrated very good cycling stability – the capacity retention values of most samples after 145 cycles were 80-90 %. The rate performance of these materials has also improved significantly in comparison with amorphous silicon inverse opals, so that capacities at 1C rate were up to 55 % of the capacities at C/10 rate.

8.8. References


CHAPTER 9.

CONCLUDING REMARKS

9.1. Preamble

In this final chapter I summarise the properties of macroporous materials synthesised and studied as lithium-ion battery anode materials, discuss similarities and differences in their electrochemical behaviour (Section 9.2).

The directions for future research of macroporous electrodes are given in Section 9.3.

9.2. Conclusion

The main goal of the research presented in this thesis has been to improve the cycling performance and rate capabilities of silicon-based electrodes for rechargeable lithium batteries. Silicon is considered one of the most promising candidates for a new generation of anode materials for lithium microbatteries due its huge theoretical capacity, attractive voltage profile, availability, low cost and compatibility with the semiconductor industry processing [1]. Colossal volume swings of electrode material during cycling, low electrical conductivity and slow lithium diffusion are the main obstacles that have been preventing implementation of silicon anodes so far.

The inverse opal structure seems to be a nearly ideal solution to at least two of the problems hindering introduction of silicon electrodes: macroporosity provides enough space to accommodate the volume changes, while thin walls greatly reduce lithium diffusion distances. The impediment of low electrical conductivity can be overcome by
combining the silicon matrix with a second, conductive material in an inverse opal structure. An obvious choice for such a material is carbon, the standard anode material in modern lithium batteries.

Electrochemical properties of five types of materials were studied: amorphous hydrogenated silicon inverse opals; nanocrystalline silicon inverse opals; carbon inverse opals; nanocrystalline silicon-carbon composite inverse opals, where carbon coating was deposited on the silicon inverse opal structure; and carbon-silicon composite inverse opals with amorphous silicon deposited on the carbon inverse opal structure.

Amorphous silicon inverse opals were synthesised by CVD into the interstices of silica opal templates and subsequent removal of the template. This material demonstrated high capacities at low currents and decent capacity retention, but its performance is severely restricted due to the low electrical conductivity of silicon.

Conversion of amorphous silicon to the nanocrystalline form by heat treatment in an inert atmosphere enhanced the conductivity of silicon inverse opals by several orders of magnitude. This led to significant improvement in discharge capacities at high rates. However, the crystalline material proved to be unstable to mechanical stresses induced by volume swings, and the inverse opal structures collapsed during cycling, leading to virtually complete loss of electrode capacity after 10-15 galvanostatic cycles.

Carbon inverse opals were synthesised by pyrolysis of a sucrose-based precursor infiltrated between the silica spheres comprising an opal structure. Carbon inverse opals demonstrated discharge capacities close to the capacities of similar materials reported in literature [2,3], excellent capacity retention and good performance at higher currents. Superb characteristics of carbon inverse opal electrodes allowed an assumption that the
combination of carbon with silicon in a macroporous structure could ameliorate cycling and rate performance of silicon.

Silicon inverse opals were infiltrated with the sucrose carbon precursor and pyrolysed to produce macroporous nanocrystalline silicon coated with a thin carbon layer. It was hoped that the carbon coating would prevent disintegration of the macroporous structure during cycling and increase the electrical conductivity of the material. Contrary to expectations, no improvement in cycling behaviour in comparison with the pristine crystalline silicon inverse opal electrodes was observed, and the macroporous structure was found to have completely collapsed after 20 galvanostatic cycles.

Another approach to the synthesis of carbon-silicon composite inverse opals was then used, whereby thin (20-100 nm) layers of silicon were deposited by CVD onto carbon inverse opals. This proved to be the ‘winning strategy,’ as such composite materials demonstrated high discharge capacities close to the capacities of pristine amorphous silicon opals, combined with the capacity retention and rate performance approaching those of carbon inverse opals.

Overall, amorphous silicon materials based on inverse opal structures demonstrated promising cycling characteristics, confirming the original idea that high macroporosity coupled with the amorphous nature of silicon might be beneficial for reducing stresses associated with large volume changes during electrochemical lithium insertion-removal. Introduction of a conductive carbon backbone into the structure led to great improvement in rate performance. The presence of carbon also decreased
pulverisation of silicon and pore clogging, hence achieving better capacity retentions after prolonged cycling.

9.3. Future Work

9.3.1. Optimisation of the carbon-silicon composite inverse opal structures

An important issue that may hinder the use of inverse opal-based materials as electrodes for lithium-ion batteries is the production cost. Indeed, nowadays commercially used anode materials such as carbon cost less than $10 per kilogram [4], and inverse opals cannot compete with this price, since just one of the starting materials – commercially available silica microspheres – costs several hundred dollars per kilogram. However, the price of the electrode material is of much less importance for the fabrication of thin film microbatteries, and an incontestable advantage of silicon-based electrodes for such devices is that their production can be relatively easily incorporated into the industrial semiconductor manufacturing.

The combination of high capacity silicon with a conductive carbon backbone in an open macroporous material proved to be a promising approach to novel advanced electrode systems. It is clear that the performance of carbon-silicon composite inverse opals can be further optimised in several ways. Firstly, the influence of carbon content on the stability and rate performance of the system should be investigated. Secondly, the relationship between optimal silicon thickness and template sphere size should be established, so that volumetric energy density is maximised without compromising the rate performance and capacity retention of the electrode. Thirdly, the influence of material composition, and of hydrogen and oxygen content in particular, on the electrochemical performance of the material needs to be studied. Fourthly, the effect of
silicon doping on the electrochemical properties of silicon inverse opal electrodes and carbon-silicon composite inverse opal electrodes is definitely worth investigating, as has been demonstrated by Takamura et al. [5].

9.3.2. Macroporous electrodes beyond silicon

Other high capacity anode materials such as tin and aluminium or multi-element alloys can be either prepared in the form of inverse opals or deposited on carbon inverse opal matrix and employed as electrodes for lithium-ion batteries. Being metallic, these materials have conductivities much higher than silicon, which can lead to better rate capabilities.

Macroporous aluminium can be prepared by metal-organic chemical vapour deposition from a variety of precursors such as alkyl alanes [6,7], alkylamine alanes [8,9] or, possibly, other precursors. CVD of tin remains a challenge due to the low melting point of the metal [10]. Alternatively, these materials can be introduced into the interstices of an opal template by electrochemical cathodic deposition [11 and references therein]. A wide variety of intermetallic alloys can also be prepared in this way.

Carbon inverse opals can also be implemented as matrices for cathode materials, whose rate performance often suffers from low electrical conductivity. The feasibility of such approach has been demonstrated by Yamada et al. [12] who coated carbon inverse opals with vanadium pentoxide. It should also be possible to synthesise composites with other cathode materials. As an example, a precursor for sol-gel synthesis of lithium iron phosphate LiFePO4 [13], one of the most promising cathode materials, could be
infiltrated into the carbon inverse opal. Pyrolysis of this system should result in LiFePO4 coating on the carbon backbone.

9.3.3. Towards microbatteries

Investigation of the electrochemical performance of a carbon-silicon composite inverse opal – solid electrolyte combination should be the next step towards implementation of microbatteries based on macroporous film electrodes. Polymer or ceramic electrolytes can be used in solid state batteries. A polymer electrolyte seems to be an optimal choice for this system as the flexible polymer should allow for better accommodation of electrode volume swings than a hard ceramic material. It might be possible to infiltrate ether-based polymer electrolyte in the interstices of a macroporous film by thermal softening. Alternatively, a polymer film can be deposited onto the inverse opal surface electrochemically [14,15]. A three-dimensionally interpenetrating solid state cell based on carbon-silicon composite inverse opal can be made analogously to the carbon inverse opal based cell fabricated by Stein and colleagues [14,15]. However, introducing enough cathode material into the system to fully utilise high capacity of silicon could prove to be challenging.

Overall, the promising cycling behaviour demonstrated by carbon-silicon composite inverse opal electrodes opens wide possibilities for modifications of this system and suggests a synthetic approach to other composite materials with exciting new properties.
9.4. References


