

ARCHITECTURE OF MESOPOROUS ELECTRODE MATERIALS

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Introduction

A novel liquid crystal template method for synthesis of nanostructured, mesoporous silica was described by Attard at the University of Southampton in 1995 [1]. Electrodeposition of platinum in a liquid crystal template [2] was presented as a general synthesis technique for metal films containing a lattice of periodic channels with nanometer dimensions. This presentation will review our progress and highlight recent developments, particularly in the area of mesoporous Ni/NiOOH which has led to the development of a high performance supercapacitor.

The principle of templated electrodeposition is illustrated in Figure 1. Following the pioneering work of Martin [3], an electrodeposition reaction is constrained to the areas of a conductive substrate material which remain exposed to the electrolyte after the application of a mask or template in intimate contact with the surface. In our work the template has consisted of a self-assembled liquid crystal phase of a surfactant such as one of the examples given in Figure 2.

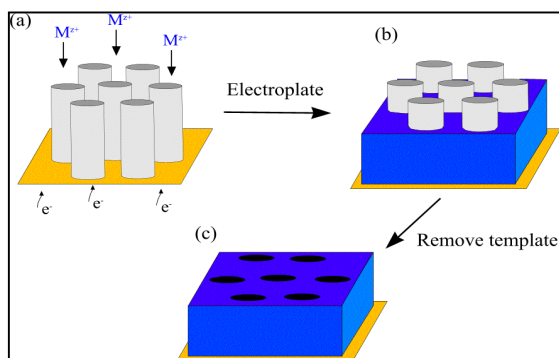


Fig. 1 *The templated electrodeposition method*

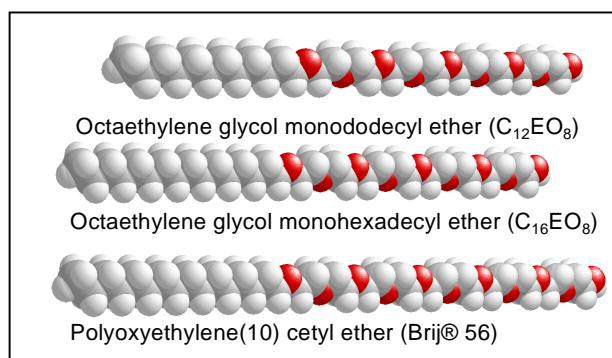


Fig. 2 *Some non-ionic surfactants used as templates*

A variety of liquid crystalline phases that can be formed from surfactant/water mixtures is illustrated, together with the phase diagram, in Figure 3. The hexagonal phase, which exists over a wide range of composition and temperature, forms a useful template consisting of long cylinders of surfactant with a uniform radius determined by the length of the surfactant molecule. With a variety of surfactants and added hydrocarbon swelling agents, the range of radii has been varied from 1.7 to 3.5 nm.

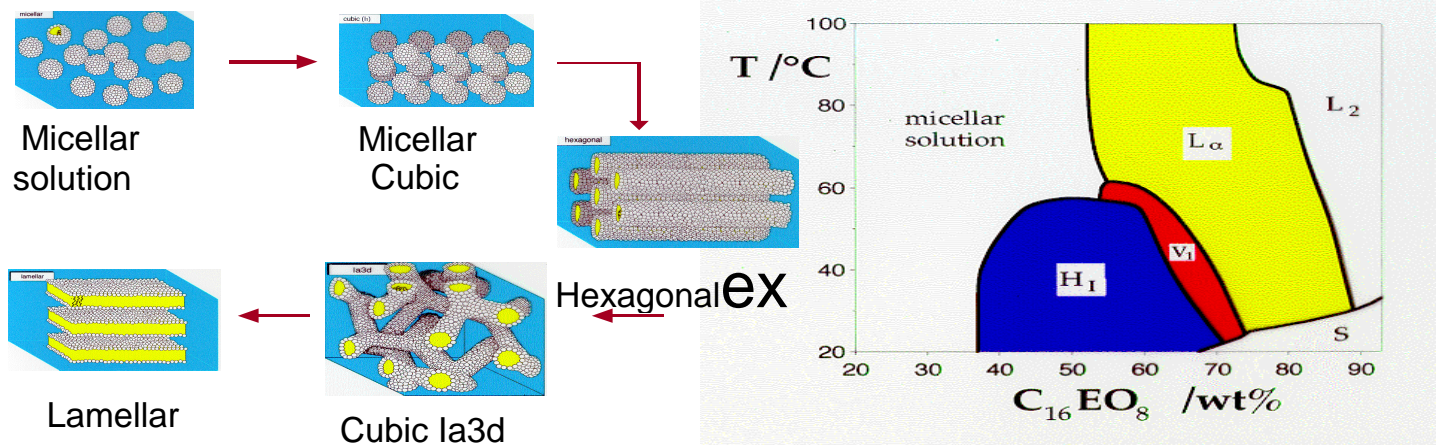


Fig 3. Schematic of liquid crystal structures and the phase diagram for the $C_{16}EO_8$ /water system.

Several deposition reactions have been used. In addition to the original sol-gel hydrolysis of alkoxides, we have used chemical redox displacement reactions such as reduction of platinum acid by iron or hydrogen. Electrochemical plating routes for production of thin films on conducting substrates have included anodic reactions and electropolymerisation in addition to normal metal plating. In total the range of materials made in nanoarchitected form includes several metals, semiconductors and alloys (Pt, Pd, Rh, Fe, Co, Ni, Cu, Sn, Pb, Ag, Se, Pt/Pd, Pt/Rh and Fe/Co) inorganic compounds (SiO_2 , AgI, MnO_2 , PbO_2 , CdSe) and organic polymers (polyacrylamine, polyphenylenediamine).

Results and characterisation of nanostructured materials

Transmission Electron Microscopy has yielded the most visually demonstrable proof that the results of template synthesis are truly nano-architected with a periodically repeating pattern of pores. (Fig. 4). Hexagonal patterns are commonly observed, and sometimes rectangular patterns, interpreted as projections of the cubic structures. TEM is, however, only suitable for observing small samples in thin section, as large parts of normal samples are impervious to the electron beam.

Small angle x-ray diffraction is a useful general technique for the observation of periodicity on the nanometer scale. However, it is rather insensitive and prone to artefacts due to the very small diffraction angles. Improvements in characterisation using diffraction will require specialised instrumentation.

Electrochemistry itself should provide the most appropriate characterisation method for nanostructured electrochemical materials. Cyclic voltammetry has been moderately successful, showing a quantitative measure of the surface area accessible, but only a qualitative assessment of the main advantage of nanostructure rather than just nanosize which is the continuity of both ionic and electronic conduction frameworks. Impedance spectroscopy has recently shown how the effective resistance to the internal surface can be measured [4].

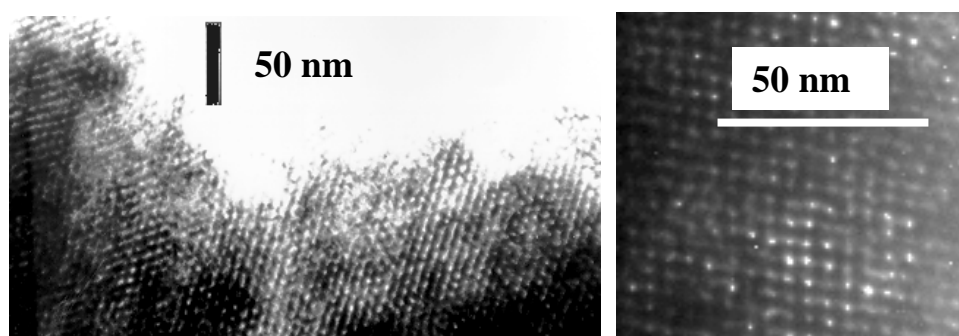


Fig. 4. TEM images of (a) hexagonal nano Pt and (b) cubic nano-Pt

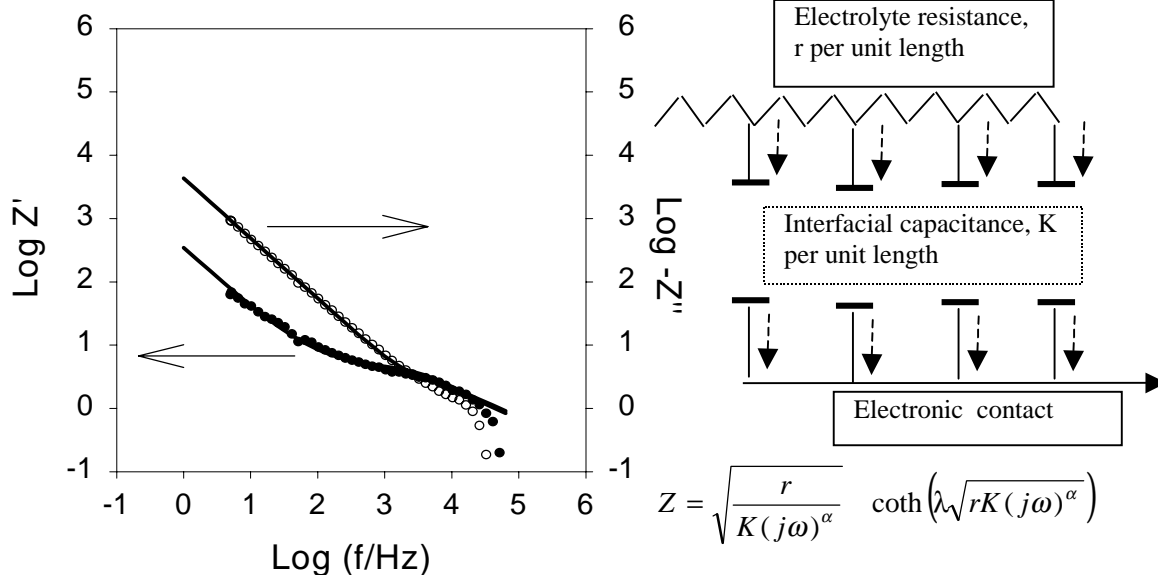


Fig. 5. Impedance data (circles) for a nanostructured Pt electrode in 1M H_2SO_4 and fit (lines) to a transmission line model (right).

Products and applications

The transition frequency for a change from diffusive to capacitive behaviour in Fig. 5 indicates a remarkably short time constant of the order of milliseconds for charging the large double layer capacitance within nanostructured Pt. Obvious applications are in supercapacitors and high rate rechargeable batteries. Very short discharge times (<50ms for 200 mC cm^{-2}) have been found for nanostructured Ni(OOH) [5]. The normal material is already a positive electrode in several nickel-based batteries and it may be expected that nanostructure will bring large increases in power density. Associated applications may be expected in electrochromic devices, in which the time constant for switching may be substantially reduced. Nanostructured forms of platinum and its alloys with specific surface areas up to 86 $\text{m}^2 \text{g}^{-1}$ are being investigated as fuel cell electrodes. Studies of CO electro-oxidation on nano-Pt [6] have shown a lower poisoning at potentials relevant to fuel cell operation. Pt/Ru alloys with specific surface areas up to 86 $\text{m}^2 \text{g}^{-1}$ have been prepared and found to give more facile CO oxidation than commercial catalysts or by mesoporous Pt [7]. New applications for sensors are suggested by the large increase in the apparent electrochemical rate constant of a nanostructured electrode and the greater resistance to fouling due to the large area of surface. A nanostructured platinum sensor for oxygen in seawater is currently under investigation [8]. Electrodeposited nanostructured palladium has been demonstrated as a superior active element of a pellistor (combustible gas sensor) for methane gas detection [9]. Other non-electrochemical applications are as heterogeneous catalysts, photovoltaics, field emitters and nanoporous magnets for non-cryogenic separation of oxygen.

Conclusion

The templated method for the synthesis of nanoarchitected materials has been generalised to produce a variety of metals, semiconductors and polymers as thin film electrode materials. The electrodes have been shown to have a large surface area accessible from both the electrolyte and the electronic contact sides. Applications are being investigated as electrodes for supercapacitors, batteries fuel cells and several other devices.

References

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