Nanostructured Materials for Batteries

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SUMMARY: Nanostructured metals can aid fast battery cycling by providing continuous paths for electron and ion transport. The novel fabrication method of liquid crystal templating has been used to make nanostructured platinum and tin as monolithic films containing hexagonal pore structures with controllable lattice parameters of about 5 nm. The pore structure leads to a surface area enhancement in platinum giving a double layer capacitance of 0.05 Fcm^{-2} and a series resistance of less than 0.005 $\Omega.cm^2$ in a 3 micron film. A similar nanostructure in tin has been shown to withstand the expansion and contraction strains during lithium cycling.

Introduction: Why Batteries Need Nanostructures

First, what do we mean by a nanostructured material? In this context it is not just poorly crystallised material, nor a composite material with discrete nano-sized solid grains as in Fig. 1(b), but a solid which has a highly organised porous architecture on the nanometer scale as illustrated in Fig. 1(c). The importance of this type of structure in electrode materials is the ideal combination of a high surface area, continuity of the solid structure and a non-tortuous open porosity. This allows optimum interaction between two phases, for example an electronic conducting metallic phase and an ionically conducting electrolyte solution filling the pores, which can lead to very fast discharge and charge rates in a battery. Fig. 1 illustrates three important types of rate limitation in a battery electrode structure as follows:

1. diffusion of ions and electrons from the outside to the inside of the electrode particles.
2. transport of electrons from the back contact to the front of the electrode
3. transport of ions from the electrolyte to the back of the electrode

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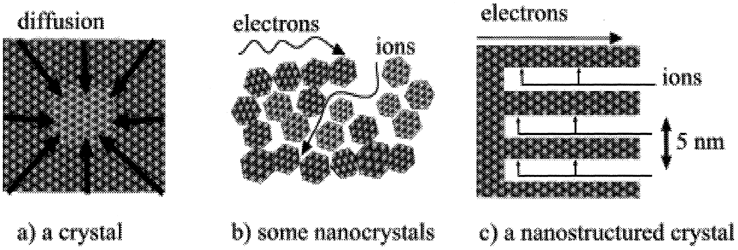


a) a crystal b) some nanocrystals c) a nanostructured crystal

Figure 1 Schematic loss of capacity due to slow diffusion in a large crystal, poor electronic contact in nanocrystalline material, but good utilisation in a nanostructure

Diffusion can limit the discharge rate of normal crystals unless the diffusion coefficient is very large. The time taken for diffusion is of the order τ, i.e.

$$\tau \approx \frac{r^2}{D} \quad \text{where r is the diffusion distance} \qquad (1)$$

In a nanocrystalline sample the diffusion distances are small but the paths for electron and ion transport are very tortuous, therefore some crystals can be excluded during a fast discharge. However, *nanostructured* electrodes provide open channels for ionic conductivity and continuous pathways for electron transport and therefore are ideal structures for electrodes. The effective diffusion coefficient in a nanostructure can be estimated from the effective ionic and electronic conductivities according to the equation,

$$D = \frac{1}{(\rho_{ionic} + \rho_{electronic})k} \qquad (2)$$

where k is the capacitance or pseudocapacitance, dQ/dE, per unit volume

This equation emphasises the need for both ionic and electronic conductivities to be optimised by having non-tortuous channels within an electronic conducting matrix with minimal grain boundary resistances. This is not the normal situation in an ordinary porous material.

Another problem with bulk electrode materials in batteries is decrepitation. Metallic tin, for example, has one of the highest theoretical capacities as a lithium storage electrode, corresponding to a limiting composition of $Li_{4.4}Sn$. Unfortunately, lithium insertion/extraction in tin is accompanied by a volume expansion/contraction of 200%, under which circumstances crystals above a certain size break apart forming a mass of disconnected nanoparticles. However, a suitably nanostructured monolithic structure may be expected to withstand the strains induced on cycling.

Until recently the optimisation of electrodes as suggested above was not possible because there was no economical method for the production of nanostructured materials. Now we have a general synthesis of mesoporous solids with a high degree of spatial order$^{1)}$ and the electrodeposition of nanostructured platinum films from the aqueous environments of lyotropic liquid crystal phases has also been described$^{2)}$. This paper will highlight the advantages of nanostructured electrodes for energy storage, with particular reference to the fast discharge of an enhanced double layer capacitance in nanostructured platinum electrodes and improved lithium cycling tolerance of nanostructured tin.

Liquid Crystal Template Synthesis of Nanostructured Materials

The template method is based on the lyotropic liquid crystal systems formed by certain long chain surfactants and water. The first example of this method used $C_{16}EO_8$, which has a long hydrophobic hydrocarbon tail attached to a hydrophilic oligoether head group.

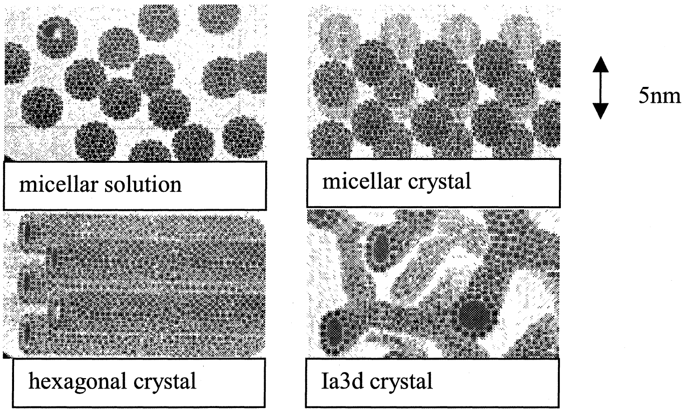


Fig.2 Self-assembly of surfactant molecules to form micelles and liquid crystals.

Solutions of this material in water which are above the critical micelle concentration form spherical micelles to minimise the solvent-solute interaction energy. At increased concentration, energy minimisation occurs in a series of liquid crystalline phases with ordered regions of surfactant breaking the aqueous region into nanostructured channels (Fig 2).

(The structure of the liquid crystal phase depends on both composition and temperature, and can be determined by polarised light microscopy; this technique detects optically anisotropic crystals which can be further identified by their texture.)

In principle, any reaction with a solid product can be performed within these channels to produce a nanostructured solid. The first reaction of this type to be demonstrated was the hydrolysis of tetraethoxysilane, TEOS:

$$Si(OEt)_4 + 2H_2O \rightarrow SiO_2 + 4EtOH \qquad (3)$$

Three new forms of silica were produced, H_I-SiO_2, Ia3d-SiO_2, and $L_\alpha SiO_2$, according to the symmetry of the precursor liquid crystal phase.

Templated Electrodeposition of Nanostructured Films

An extension of the above technique was electrodeposition in a nanostructured electrolyte. The electrolyte was formed by dissolving chloroplatinic acid, H_2PtCl_6, in water prior to mixing with the surfactant $C_{16}EO_8$ (98%,Fluka). The phase diagram is favourably different from that in pure water, showing an extended hexagonal domain stable up to $100^{O}C$.

Electrodeposition onto a gold coated glass slide was carried out using a 3-electrode arrangement in a small thermostatted cell.. The overall reaction was assumed to proceed as follows:

$$H_2PtCl_6 + 4e^- \rightarrow Pt + 2H^+ + 6Cl^- \qquad (4)$$

On disassembly of the cell and washing with deionised water the product was seen to be surprisingly bright and shiny compared with the platinum black deposits typically produced from aqueous solutions of hexachloroplatinic acid without the surfactant added.

A similar experiment was carried out using a solution of tin sulphate, $SnSO_4$ mixed with surfactant in order to deposit films of nanostructured tin in a thin cell, sandwiching the templated electrolyte between two smooth electrode surfaces: a tin counter electrode and a copper or gold working electrode was used. The cell reaction was assumed to be:

$$SnSO_4 + 2e^- \rightarrow Sn + SO_4^{2-} \qquad (5)$$

In this case the rather expensive $C_{16}EO_8$ was sometimes replaced by a commercial surfactant, Brij 76 (Aldrich), which has the approximate composition $C_{18}EO_{10}$. Heptane was also sometimes added to expand the pore size of the nanostructure by dissolution in the hydrophobic regions.

Films were physically characterised by SEM, STM, TEM and small angle x-ray diffraction to evaluate the effect of the template.

Electrochemical characterisation took the form of cyclic voltammetry and impedance analysis in dilute sulphuric acid in the case of platinum films, 1M lithium triflate in ethylene carbonate/diethyl carbonate in the case of tin. Further characterisation of the tin samples was carried out by lithium cycling in the same electrolyte.

Results and Discussion

Characterisation of the platinum deposits by scanning electron microscopy showed very smooth and uniform films with the only surface detail being due to the underlying substrate. Scanning tunnelling microscopy at high magnification with z-axis expansion showed the undulating gold surface of a sample to be covered in a structured nanoporous layer (Fig. 3a). Parts of films removed from substrates and examined in TEM revealed highly organised, long range, hexagonal structures confirming that the deposit was indeed formed around an intact liquid crystal template

(Fig. 3b). The dimensions of the nanostructures could be measured accurately from the TEM, indicating separations between the pore centres of between 5 and 7 nm, depending on the composition of the surfactant. The minimum wall thicknesses between the vacant cylinders were estimated to be around 2.5nm.

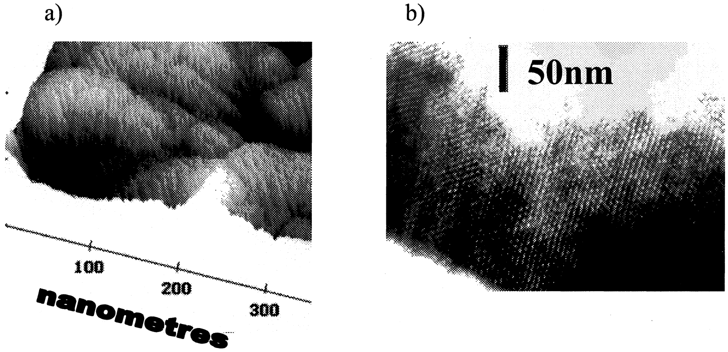


Figure 3. (a) STM and (b) TEM of a nanostructured platinum film

TEM images obtained for tin deposited in the liquid crystal templates were not as impressive as those obtained for platinum and are shown in Fig. 4(a). However, small angle x-ray diffraction analysis (Fig. 4(b)) of many samples indicated mesoporous products by peaks occurring at 2θ =1.4° ±0.1°, corresponding to a repeat distance of about 6.5nm ± 0.5nm.

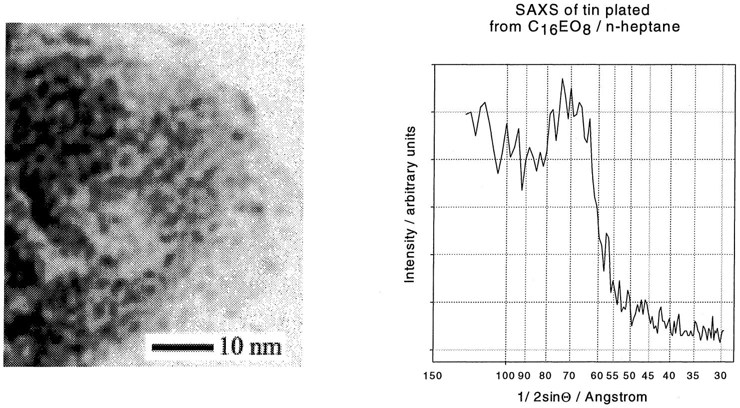
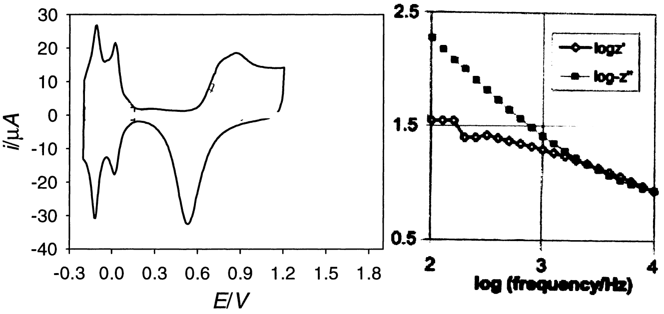


Figure 4. (a) TEM and (b) Small angle x-ray diffraction of a templated tin film

Electrochemical characterisation of the platinum films is illustrated in Fig.5. The cyclic voltammogram resembles the well known result for a clean polycrystalline surface in sulphuric acid and the processes of double layer charging and reversible hydrogen adsorption are well resolved. However, the current corresponds to a surface area about 300 times greater than the superficial area. Results taken over a variety of deposition conditions showed that the samples have an intricate open porosity, corresponding to between 65 and 130% of the theoretical surface area of 360 km^2 m^{-3} calculated for a hexagonal nanostructure with dimensions given above.

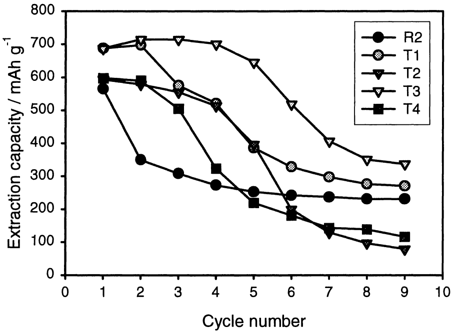


E= 0.2 V vs SCE
A= 3x10^{-4}cm^2
Thickness= 3μm
(2 electrodes in series)

Fig 5 (a) cyclic voltammogram and (b) impedance of nanostructured platinum

The complex impedance spectrum for a 2-electrode cell with nano-Pt electrodes in 1M sulphuric acid, Fig 5b, shows a similar surface area enhancement from the frequency dependence of the reactance. A capacitance of 50mFcm^{-2}, equivalent to a volumetric capacitance of 170 Fcm^{-3} for a 3-micron film is shown by a slope of unity at low frequency, whereas at high frequency the diffusive behaviour of equation 2 is illustrated by a slope of 0.5. An effective series resistance of only 5 mΩ cm^2 showed that the paths for conduction are relatively continuous in both the electrolyte and the electronic conducting matrix, and a rough calculation of the effective conductivity gives a value of about 60 mS cm^{-1}. The calculated effective diffusion coefficient of 3 x 10^{-4} cm^2 s^{-1} is impressive, as is the ability to deliver the high capacitance at frequencies above 1kHz.

In the case of the tin films the main goal was to demonstrate a tolerance to lithium cycling without decrepitation. Fig. 6 illustrates the retention of discharge capacity after the first cycle in a series of nanostructured electrodes as compared with a smooth deposit, which degrades on decrepitation. The best capacity value of 700 mAh.g^{-1} may be compared with the value of 372 mAh.g^{-1} for graphite as used in some commercial lithium batteries.



R2 – smooth deposit from a non-templating reference electrolyte

T1- templated from $C_{16}EO_8$
T2- templated from Brij76
T3- templated from $C_{16}EO_8$ with 5w/o added heptane
T4 – templated from Brij76 with 3.5w/o heptane

Fig. 6. Lithium extraction capacity of nanostructured *vs* smooth tin

Conclusion

This work has demonstrated that liquid crystal templating during electrodeposition can lead to nanostructured electrodes with a high continuity of electronic and ionic conduction paths. The nanostructural form has been shown to give a highly accessible surface capacitance in the case of platinum and a resistance to decrepitation in the case of lithium insertion in tin. These results are considered to be general and applicable to many battery materials.

References

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Acknowledgements

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