Using Polymer Templated Nanoporous Materials to Improve Performance in Electrochemical Pseudocapacitors and Batteries

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INTRODUCTION

Improving performance in batteries and supercapacitors is an important part of solving the energy problem faced by the world today. Both higher capacity batteries and systems capable of faster charge and discharge are needed. Because of their unique combination of high surface area, open and interconnected porosity to facilitate solvent diffusion, and mechanical flexibility, periodic nanoporous materials hold exciting promise for solving these problems. In this talk, we will address two charge storage systems that exploit these unique properties of block copolymer template nanoporous materials.

In the first case, we focus on electrochemical supercapacitors produced by polymer templating of both sol-gel\textsuperscript{1} type and nanocrystal building blocks.\textsuperscript{2} Capacitive energy storage is distinguished from other types of electrochemical energy storage by short charging times and the ability to deliver high power density. A key limitation to this technology is its low energy density, however, and for this reason there is considerable interest in exploring pseudocapacitive charge storage mechanisms which utilize battery like redox reactions at the surface of a porous material. Here, pseudocapacitive materials are produced through block co-polymer templating methods in which inorganic precursors are co-assembled with diblock copolymers. We find that nanoporous materials built from nanoparticle building blocks effectively combine the high surface area of small nanoparticle based solids\textsuperscript{3} with the efficient solvent diffusion of large mesoporous materials and thus show high levels of capacitive charge storage, even when the parent metal oxide does not show efficient Li\textsuperscript{+} diffusion in the bulk.\textsuperscript{3}

To improve capacity, rather than rate performance, we move to ultra-high capacity anode materials. Silicon, in particular, show remarkable capacity as an anode for Li\textsuperscript{+} batteries, but very poor cycle life and poor rate capability in bulk form. The poor cycle life arises because of a \textasciitilde400% volume expansion that occurs upon alloying with lithium. Periodic porous materials can show remarkable mechanical flexibility, simulating a nanotuss architecture.\textsuperscript{4} This flexibility can significantly improve cycling performance in nanoporous silicon anodes.

RESULTS AND DISCUSSION

Nanoporous supercapacitors can be synthesized from nanocrystal building blocks using block copolymer templating methods. Generalized synthetic routes involve first stripping the ligands from the nanocrystals and then co-assembling the nanocrystals with an amphiphilic diblock copolymer. A broad range of polymer can be used, but most contain one poly(ethylene oxide) block and one hydrophobic block. Figure 1 shows a generalized scheme for the production of nanocrystal based nanoporous materials.

![Figure 1. Schematic of the polymer templating process. Either molecular precursors or preformed nanocrystals can be co-assembled with the block-copolymer to produce a periodic nanoporous material.](image)

Figures 2 and 3 show examples of SEM images of nanocrystal based nanoporous materials that can be produced using these methods. Figure 1 shows an example of nanocrystal based nanoporous titania, while figure 2 shows an example of a nanoporous manganese/iron oxide. While neither of these oxides show particularly fast lithium ion insertion in bulk form, we find that fully half of the total stored charge is not diffusion controlled (i.e. kinetically fast) in the nanocrystal based nanoporous materials shown below at slow sweep rates. As the sweep rate is increased, intercalation processes become kinetically limited, and the charge storage becomes increasing dominated by pseudocapacitance.

![Figure 2. SEM image of a nanoporous titania film produce via polymer templating of preformed, ligand stripped titania nanocrystals.](image)

![Figure 3. SEM image of a nanoporous manganese, iron oxide film produce via polymer templating of preformed ligand stripped nanocrystals.](image)
shown above. The ability to produce composite electrodes with some components optimized for electrical conductivity and some components optimized for redox activity illustrates the power of these nanocrystal based nanoporous architectures.

For silicon based materials, we move away from nanocrystal templating, and instead relay on magnesium based reduction of more conventional block co-polymer template sol-gel silica (SiO\(_2\)) materials to produce our starting materials. Figure 4 shows an SEM image of nanoporous silicon produced in this way. The periodic porous architecture is maintained, despite the high temperature process and harsh chemical conditions used to convert silica to silicon.

![Figure 4](image)

**Figure 4.** SEM image Nanoporous Si produce via reduction of template porous SiO\(_2\).

We find that this porous silicon shows a unique combination of good cycle life and much fast rate performance that that observed in other forms of bulk or nanoscale silicon. Good capacity retention is observed at galvanostatic charge/discharge rates as fast as 10C. The improved performance likely arises from the high surface area, short solid state diffusion lengths, and robust mechanical behavior that can be found in ordered nanoporous materials.

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**REFERENCES**