ON THE CORRELATION BETWEEN MECHANICAL FLEXIBILITY AND NANOSCALE STRUCTURE IN SELF-ASSEMBLED POROUS FILMS WITH NANOCRYSTALLINE WALLS - FROM BATTERIES TO CAPACITORS

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Surfactant and polymer templating is a powerful tool that has been widely used to produce inorganic powder materials with periodicities in the sub-30 nm size range. The corresponding thin films can be achieved by the same coassembly methods but using an evaporation-induced self-assembly (EISA) process [1]. This process was introduced by Ogawa and Brinker in the late 1990’s and is still the method of choice in the preparation of inorganic thin films with nanoscale periodicity. In recent years, it has been shown that classical sol-gel techniques can be used to produce a wide variety of redox active materials that lend themselves for high rate rechargeable lithium batteries. However, the use of EISA to synthesize such materials in thin film format with both a well-defined mesoporous morphology and nanocrystalline framework has not yet been reported. Part of the reason for this is the fact that the majority of the polymers used to template materials do not allow the inorganic walls to be crystallized while retaining nanoscale order (due to the mismatch between critical nucleation size and pore wall thickness). In this work, we incorporate novel diblock copolymers, such as poly(ethylene-co-butylene)-block-poly(ethylene oxide) and polyisobutylene-block-poly(ethylene oxide), as structure-directing agents. These porogens have been shown to be highly suitable for the direct synthesis of oxide thin films with cubic networks of pores averaging 15-25 nm in diameter. The large distances involved accommodate walls sufficiently thick to allow for uniform nucleation and growth of the crystalline phase with retention of the periodicity. Thus, by adjusting different processing parameters, such as the relative humidity and polymer-to-precursor ratio, it is possible to get access to a broad range of inorganic architectures with open mesopore cavities.

In this work, we aim at exploiting redox active materials with ordered large-pore mesoporous structures for energy storage applications. Through these experiments, the relationships among nanoscale structure, charge storage and mechanical flexibility are examined and compared to non-templated samples [2]. By correlating mechanical changes with redox activity, we are able to identify some of the unique advantages of using nanoporous architectures for electrochemical materials. We note that most of the redox active oxides are quite rigid in the bulk crystalline form and thus there is the prospect of tuning the mechanical response by the formation of an architecture with periodic nanoscale porosity.

Unlike many traditional battery materials, oxides like AMoO₄ (A = Ca, Co, Mg, Ni), α-Fe₂O₃, and NiFe₂O₄ do not have a layered or tunnel structure. As a result, electrochemical redox reaction rates in the bulk material are quite slow, which limits their usefulness for electrochemical charge storage devices. Our preliminary results, however, show that nanoporous versions of these materials exhibit reasonable levels of pseudocapacitive charge storage and much higher capacities than samples prepared without any polymer template [3,4]. We assume that part of the increased capacity stems from the fact that these thin film electrodes are able to expand normal to the substrate upon lithiation by flexing of the nanoscale pores. This flexing may relieve stress from volume expansion that normally inhibits charge storage, as shown recently [2,5].
To probe the mesoporous architectures both grazing incidence small-angle X-ray scattering (GISAXS) and *in-situ* SAXS in transmission mode were used. The GISAXS patterns shown in Figure 1 were collected at an angle of incidence $\beta = 0.2^\circ$ on beamline BW4. GISAXS, in general, provides insight into the in- and out-of-plane periodicity of self-assembled thin films and thus allows for a thorough characterization of the pore network, which, in turn, makes this technique invaluable to the nanomaterial community. During the synchrotron runs in 2010, we systematically studied the nanoscale periodicity as a function of annealing temperature and examined the impact of both the polymer-to-precursor ratio and relative humidity on pore ordering and symmetry. We found that (1) the relative humidity plays a decisive role in the self-assembly process of the above mentioned materials, (2) the pore sizes can be readily tuned from some 10 nm to ~30 nm, and that (3) the initially amorphous framework structures can be fully crystallized while retaining nanoscale porosity (see SEM images in Figure 1). Overall, these experiments establish that all of these materials can effectively withstand the stress that develops over the course of thermal treatment, in particular those associated with the crystallization. Moreover, *in-situ* SAXS revealed that the coassembly process is typically completed after ~60 seconds and leads to distorted f-c-c pore networks with (111) orientation relative to the plane of the substrate.

Future GISAXS experiments at BW4 will be dedicated to address the following question: “what is the correlation between the out-of-plane film deformation and changes in the in-plane stress”. While changes in pore structure are usually rather difficult to measure, a well-defined pore network provides an opportunity to follow small changes in the periodic system [2].

![Image](image.png)

**Figure 1:** (a,b) GISAXS patterns obtained on a mesoporous NiFe$_2$O$_4$ spinel thin film showing the evolution of the distorted f-c-c pore network with (111) orientation upon thermal treatment. Scattering vector, $s$, components are given in 1/nm. (c-f) Morphology of polymer-templated NiFe$_2$O$_4$ (c,d) and $\alpha$-Fe$_2$O$_3$ (e,f) thin films before and after lithiation.

**References**