Ordered vanadium oxide inverted opal Li-ion battery electrodes and optical probing of phase changes

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Bicontinuous three-dimensionally ordered macroporous (3DOM) electrode designs are currently showing great promise as interconnected architectures for lithium ion battery electodes (1, 2). Vanadium oxide inverted opals have in particular proven successful for overcoming some of the rate challenges faced by the normally poorly conductive material. The 3DOM or inverted opal architecture has been demonstrated (3-5) to offer improvements in both power and energy density due in most part to the continuous network of electrode material, the large interfacial area and the open access for lithium insertion (6). The unique optical properties derived from the periodic nature of these 3DOM structures allow for spectroscopic analysis techniques into the order and structural integrity of the materials (7-9). The photonic band gap (PBG) for 3DOM materials is strongly sensitive to disorder and by monitoring the PBG before and after charging and discharging the change in structure and order can be assessed. By combining this non-destructive structural dependent technique and electron microscopy, we show how changes in structural quality and order are related to lithium insertion and removal processes in the battery cathode.

Here, we demonstrate well-ordered 2D and 3D inverted opal structures of vanadium oxide from a mono-layered and 3DOM colloidal PS/PMMA sphere templates, shown in Fig. 1, by selected infilling techniques. The light scattering properties of mono-layered templates before infilling are compared to infilled inverted opal V_2O_5 structures (Fig. 2). The 2D light scattering ability of mono-layered inverted opals (Fig. 1b) is shown to be useful for monitoring structural changes caused by changes to refractive index, periodicity, order and crystal structure. Comparisons of the reflection and diffraction properties of the inverted opals before and after charge-discharge tests as a Li-ion battery electrode will be discussed. Importantly, the relationship between the structure and changes in crystallinity on the overall electrochemical behavior of both ordered and disordered materials will be shown.

The dependence of order in the electrode material will be examined using electron microscopy and spectroscopic monitoring of reflection and PBG. This allows us to determine the extent of the influence of structural changes to cyclic lithium insertion and removal where considerable material volume changes and stresses are known to limit charge capacity and cycle life in many Li-ion battery materials. We debate the ability for ordered crystalline inverted opals to minimize this volumetric expansion by allowing the material space to deform and grow and relate this to disordered inverted opals that have no preferred direction for crack propagation or deformation. The lack of order will limit the usefulness of the optical experiments however, for these cases phase and microscopy information will be related to the battery performance.

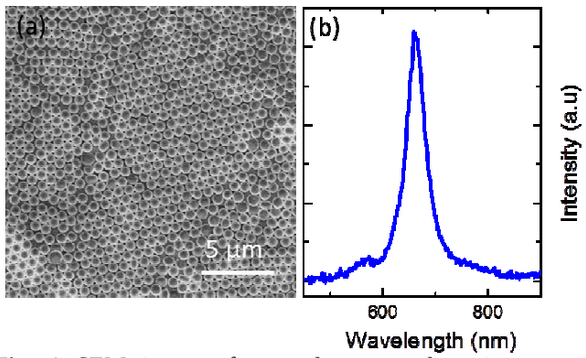

Fig. 1 SEM image of mono-layer template, i.e. one without a 3DOM photo band-gap, before infilling of electrode material and first order planar diffraction at an angle β≈20° from the same template for an incident angle of 45°. This scattering ability may disappear on infilling of vanadium oxide precursor.

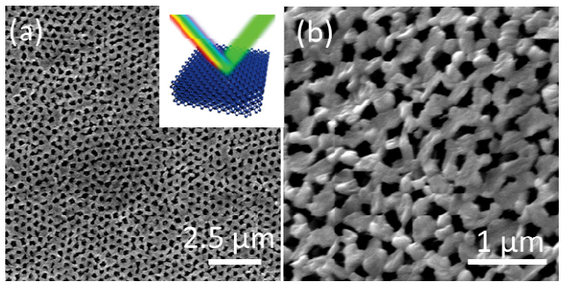

Fig. 2 SEM of disordered V_2O_5 thick walled inverted opals drop-casted from a dried-sphere and vanadium precursor mixture i.e. without a preliminary template (b) SEM at higher magnification showing disorder and varied diameter of the pores. Inset of (a) highlights the desired effect when light is reflected from an ordered inverted opals at a particular wavelength(10)

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