

Investigations into structure and chemistry of 1D, 2D and 3D structured vanadium oxide nanomaterials for Li-ion batteries

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Vanadium oxide (V_2O_5) is continuously gaining potential as a replacement cathode material in lithium ion batteries due primarily to its layered geometry, low cost and high specific capacity (1). It can also withstand high rate intercalation when the c-axis of its unit cell structure is minimized allowing high rate and fully reversible charge-discharge performance (2). It has also been successfully used in Na-ion battery electrodes (3). Three dimensional macroporous (3DOM) structures are also increasing in interest in many fields, due to their open but interconnected architecture (4). The 3DOM morphology, which can be synthesized and crystallized as a 2D monolayer or stacked 3D porous crystal with random order or crystalline order, offers some new opportunities in the development of high performance Li-ion cathode architectures through the substantial improvements in both power and rate capabilities provided by the increased infiltration of electrolyte and shortening of both electronic and ionic pathways (5). There has been some success in using these structural advantages to tackle the limited conductivity issues faced by V_2O_5 by creating a continuous network of porous vanadium oxide material, small in size but large in surface area, with shortened lithium diffusion distances and improved rate performance (6-8).

Here, we investigate the synthesis of inverted opal-type structures of vanadium oxide using polymer sphere templates and infiltration by vanadium-containing precursors. We present a microscopy-based structural and crystallographic analysis of the variation in vanadium oxide structures gained throughout the process dependent on template removal, crystallization temperature and material infilling chemistry. We compare the use of both 2D and 3D partially ordered templates and characterize the resultant electrode composition and arrangement post infiltration and calcination for various procedures.

Some examples of the sample variations obtained can be seen in Fig. 1. Drop-casting a solution of dried PS spheres mixed with a vanadium isopropoxide and isopropanol mixture and removing the spheres by calcination produces primarily disordered V_2O_5 inverted structures with thick walls, Fig.1(a). After centrifugation of a similar mixture and the subsequent calcination of the spheres V_2O_5 nanowires as seen by Fig. 1(b), were formed. Structural integrity and shape is seen to be largely dependent on calcination conditions, both ramp rate and temperature. We look at idealizing these for structurally stable inverted opal crystalline V_2O_5 which maintain order post calcination. Fig.2 shows an example of the structure formed after infilling of a sphere template by drop-cast during sonication and calcination at 450°C, a high enough temperature to crystallize V_2O_5 but in some cases not enough to burn off the sphere's completely. The effects of non-ideal conditions are seen in Fig.2(a) with the formation of a thin, patched, partially inverted structure

with poor uniformity and a breakdown in network cohesion, Fig.2(b).

The electrochemical lithium intercalation behavior of select structures is also discussed, and through correlation of structural changes after battery testing, we show, using scanning and transmission electron microscopy and angle resolved spectroscopy, how the dimensionality and order in the structures influences electrochemical lithiation. The V_2O_5 structures and morphology changes during lithium insertion and removal will also be presented as a function of cycle life and rate performance.

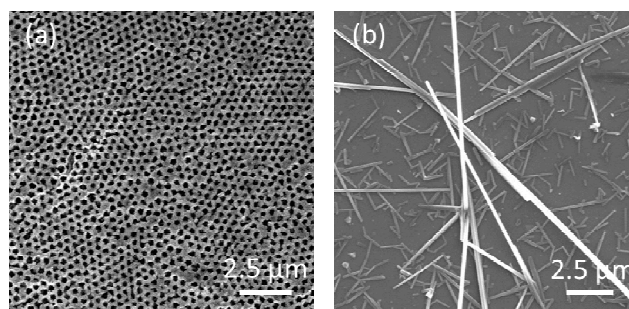


Fig. 1 (a) Thick-walled Inverted partially-ordered opal structure of crystalline V_2O_5 (b) V_2O_5 nanowires

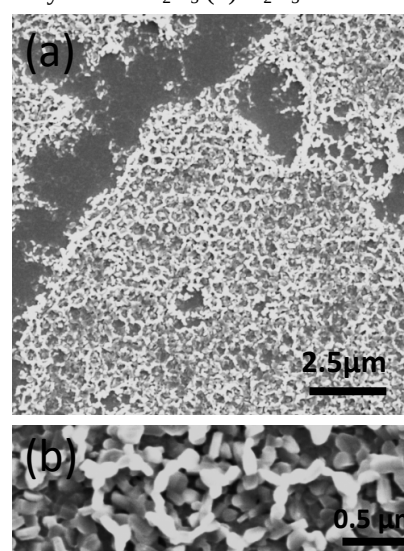


Fig 2. (a) Patched thin-layered disordered inverted V_2O_5 formed from drop-casting under sonication and calcination at 450°C (b) the non-uniform, broken, pellet-like make-up of the pore walls indicating the breakdown in order.

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