3D open-worked inverse opal TiO_2 and GeO_2 materials for long life, high capacity Li-ion battery anodes

David McNulty[a], Alex Lonergan[a], Sally O'Hanlon[a], Colm O'Dwyer[a,b,*]

[a] *School of Chemistry, University College Cork, Cork T12 YN60, Ireland*
[b] *Micro-Nano Systems Centre, Tyndall National Institute, Lee Maltings, Cork T12 R5CP, Ireland*

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ABSTRACT

In this short review, we overview some advancements made in Li-ion battery anode development, where the structural arrangement of the material plays an important role. Specifically, we summarise the benefits of 3D macroporous structure imposed the anode material, in order to improve ionic and electronic conductivity in the absence of conductive additives and binders. Two anode materials are overviewed: TiO_2 and GeO_2. These are either high capacity anode materials or accessible, abundant materials that are capable of very stable and long-term cycling. We have focused this review on 3D inverse opal structures of these anodes and summarise their enhanced behaviour by comparing their performance metrics to a range of nanoscale and porous analogues of these materials.

1. Introduction

The market for Li-ion batteries for consumer electronics and related items is expected to soar by a factor of > 60 between 2012 and 2020, rising to $3.6bn a year according to a new report from research firm HIS and others [1,2]. Underlying almost all Li-ion batteries are basic challenges [3–5] concerning the materials that are used [6]. Researchers [7,8], including our group [9,10], have identified materials that can store more energy than conventional technology [11], but the material swells significantly when fully charged then shrinks again during discharge [4,12]. This swelling and shrinking quickly breaks down the electrical contacts in some materials, contributing to capacity fading, reduction in voltage and energy. Our approach, in tandem with many other approaches worldwide, [13] is to advance the use of hierarchical, ordered porous materials [14–16] whose crystal structure is designed to remove heterogeneities in volume changes throughout the material, and increase energy density to offset lower volumetric energy density. Importantly, electrical conductivity is not adversely affected and long-term cycling is very stable.

Electrode materials for Li-ion batteries store electrochemical charge by intercalating lithium ions into the lattices of crystalline solids and into disordered vacancies within amorphous hosts. New materials on the nanoscale tackle the slow kinetics of solid-state ion diffusion into bulk electrode materials and have improved capacity retention. Essentially, these limits on ionic mobility are at least partially overcome by fabricating battery components that have solid-state ion diffusion path lengths on a nanometer-length scale. We recently surveyed many promising materials and nanoscale sizes for emerging battery constructs, and engineering material structure from the atomic scale to the electrode scale are crucial for future advances in energy storage [10,17]. In batteries, separate conductive additives and binders etc. add significant 'dead weight'. To get a high volume fraction of nanostructured active material on a surface with efficient ion and electron pathways, reducing the complexity and additives within the random network of active material is required. To do this, we can remove conductive additives such as carbons, and non-recyclable polymeric binders used stitch all materials together as the electrode slurry, to improve the gravimetric energy density of active material. This helps to regain some gravimetric capacity losses caused by the multi-functional porosity. An ordered, porous material can potentially allow fast charging and alleviate material breakup during many charge cycles.

The ordered porous 3D material architecture provides definable short electron and ion transport lengths in the active material and electrolyte (yielding high-power density) while maintaining a high volume of active material (maintaining high-energy density) [14,18,19]. Rates from several hundred C up to 1000 C (~ 4 s) for lithium-ion chemistries could potentially be achieved, enabling fabrication of a lithium-ion material that can be fully charged in a matter of minutes or seconds. Nanotechnology together with carbon coating has provided some possibilities for these requirements in standard battery architectures [20,21]. Inverse opals and other nanomaterials have successfully improved the power density of lithium-ion electrodes when
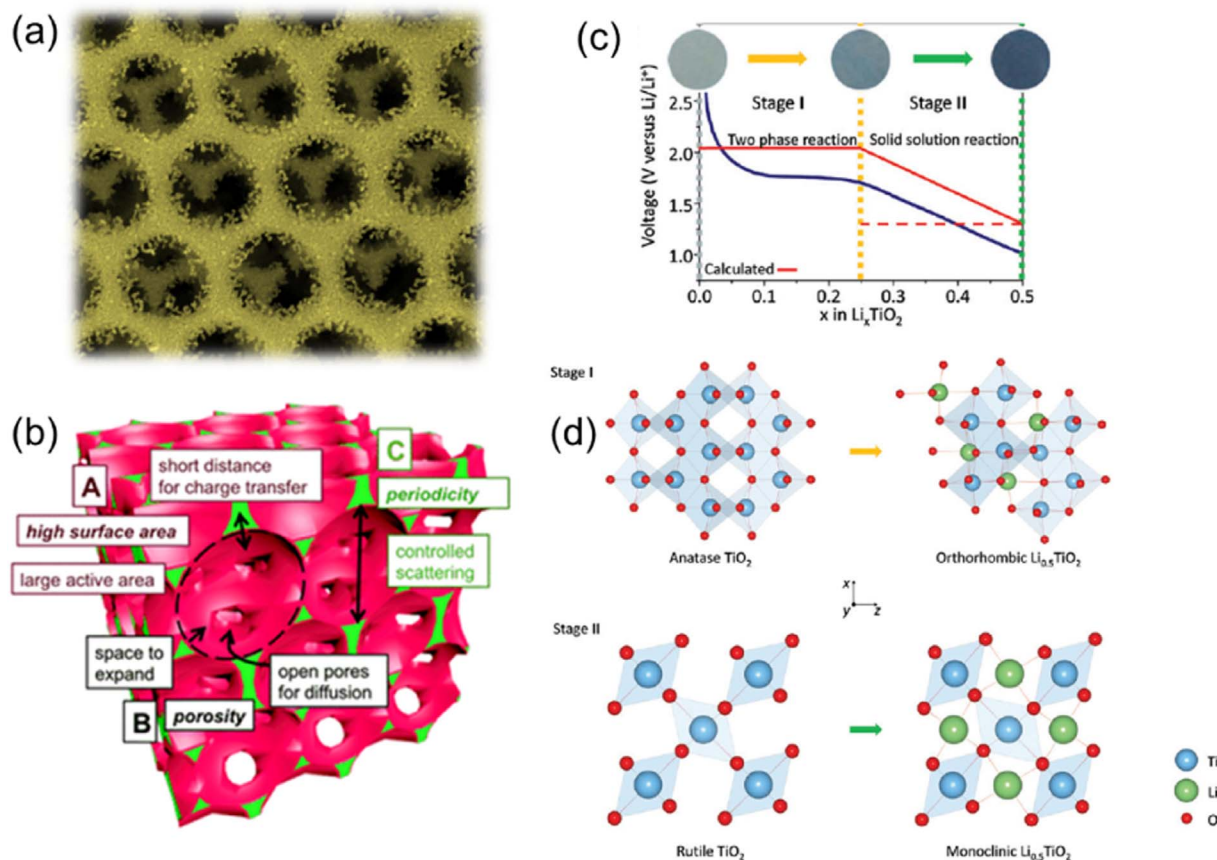
Fig. 1. (a) Typical morphology of an inverse opal metal oxide, formed from an inverse replica of a colloidal opal template. (b) Schematic representation highlighting beneficial features of a 3D macroporous interconnected active materials. (c) Measured and calculated charge profile (anode) for mixed anatase/rutile ordered porous nanotube layer material showing two regions associated with intercalation and solid solution reactions with lithium as a function of Li mole fraction [64]. (d) Summary of Li-induced phase changes from tetragonal anatase and rutile TiO_2, reproduced from Ref. [64].

used in powder form.

With respect to inverse opals, three-dimensionally interconnected macropores facilitate the rapid flux of liquid electrolyte solutions, such that several hundred $m^2\,g^{-1}$ of electrode interfaces are simultaneously accessible to lithium of other mobile ionic charges. This degree of macropore interconnectivity is intentionally tailored from self-assembled close-packed templates [22]. For example, the ionic conductivity of a 1 M $LiPF_6$ liquid electrolyte solution is only impeded by a factor of two when ion transport occurs through the interconnected macropores of monolithic carbon inverse opals (electrode thicknesses: 300 μm–3 mm). For these materials, fast transport kinetics have been achieved in one dimensional (1D) carbon nanotube- and two dimensional (2D) graphene nanosheet-based hybrid electrodes [23]. However in 1D and 2D electrodes, the fast electron transport is restricted at least in one dimension because of the structural anisotropy of the electrodes [24,25]. As a result, that dimension constrains the ambipolar (ionic and electronic) diffusion, eventually slowing down the transport kinetics in the entire battery. Such kinetics problems become more severe at high current densities (rates).

Macroporous lithium ion electrodes methods developed fabricated by Stein [26–30] and Dunn [31] over two decades ago by means of colloid templating, reduce the ion transport length and are particularly promising. However, the relatively low electrical conductivity of the macroporous host can limit the rate performance; changes to the very material as well as its structuring are also needed. Several excellent reviews and key reports summarizing scientific and performance indicators for Li-ion electrode materials templated with colloidal crystals are available [32–34].

In this short review, we summarise the most recent advances in binder-free, conductive additive-free, structured porous inverse opal anodes materials for Li- ion batteries. We survey TiO_2 and GeO_2 materials and compare some of the promising performance metrics of these materials in terms of specific capacity and long cycle life.

2. TiO_2 Anode materials

In recent years, titanium dioxide (TiO_2) has been the subject of a tremendous research effort due to its unique properties such as low environmental impact and cost, safety, and stability which make it useful for a wide range of applications including photocatalysis [35,36], sensors [37,38], drug delivery and energy storage [39–42]. Consequently, a great number of TiO_2 based nanostructures have been reported over the last decade such as nanowires, nanorods, nanoparticles and nanoflowers [43–46]. TiO_2 has also attracted a lot of attention as an intercalation mode anode material for Li-ion batteries, being a low voltage insertion host for Li^+ and as a fast Li^+ insertion/removal host [47,48]. Anatase, rutile, and TiO_2(B) with varying nanostructure architectures have been investigated as anode materials for lithium ion batteries [49–51]. Previous reports have indicated that TiO_2 nanostructures demonstrate poor performance at high rates as well as poor long-term cycling performance due to issues including the inherent low conductivity of semiconducting TiO_2 materials and volume changes associated with the insertion and removal of Li^+ [52–55]. To improve the electrochemical performance of TiO_2 anode materials there have been many reports on the combination of TiO_2 with highly conductive materials such as composites with carbon nanotubes (CNTs) or graphene and the coating of TiO_2 nanostructures with graphitic carbon [52,56,57]. However the TiO_2 component of composites still suffer