Aqueous Synthesized Mixed-Phase Brookite, Rutile and Anatase Nano-titania (TiO_2) and their Lithium-ion Storage Properties

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Mixed-phase brookite, rutile, and anatase nano-titania (TiO_2) are synthesized via a novel, high throughput process, and their lithium-ion intercalation properties are examined and compared to commercial benchmark materials. The synthesis involves processing of variable concentration $TiCl_4$ solution in a continuous-stirred tank reactor at 80°C. The new CSTR process is based on the earlier batch-reactor solution synthesis work of Charbonneau et al [1]. By modifying the concentration of the $TiCl_4$ solution, reaction time, and pH, different TiO_2 phase nanoparticles can be produced without having to resort to sol-gel or hydrothermal procedures that are less amenable to scale-up [2, 3]. A very exciting outcome of this synthesis route is that brookite [2], in addition to rutile or anatase, can be produced, hence the undertaking of the present study to evaluate and compare its Li-ion intercalation properties with those of the better studied anatase. Nano-rutile recently has been shown to have potentially interesting lithium-ion storage properties as well, hence its inclusion in this study [3].

The two TiO_2 varieties were not made of pure phase brookite or rutile but were of mixed phase content with one of the phases being ~70% of the total TiO_2. Both varieties have high surface areas (>125 m^2g^{-1}) and BET-derived crystallite sizes of ~10 nm. The morphologies of the phases differ, namely 2-D brookite nanosheets (Figure 1), and mesoporous 3-D rutile nanoparticles (Figure 2). The rutile phase mixture also shows the presence of nano-needles also seen in Figure 2. The new nano-TiO_2 varieties are compared to commercial, phase-pure anatase nanomaterials (15 nm) and P25 (30 nm) mixed-phase (anatase-rutile) particles, respectively.

The nano-titania materials were built into electrodes using 80 wt% active material, 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride (PVDF) mixed in n-methyl 2-pyrrolidone (NMP) to form a slurry. The slurry was doctor bladed onto an aluminum foil substrate that had been previously treated with 10% NaOH solution to increase film adhesion. For cyclic voltammetry, the substrate used was NaOH treated aluminum sheet.

Electrochemical characterization included cyclic voltammetry and galvanostatic cycling. Initial electrochemical testing shows that both types of mixed-phase nanotitania (brookite and rutile) to exhibit good Li-ion storage properties but with some differences in terms of capacity and cyclability that are discussed on the basis of mechanism of storage: intercalation vs. pseudocapacitance. Based on the lithiation curves, the bulk of storage capacities come from surface-area dependent processes. While some diffusional intercalation occurs, the surface area control can indicate that extremely fast charge/discharge is possible.

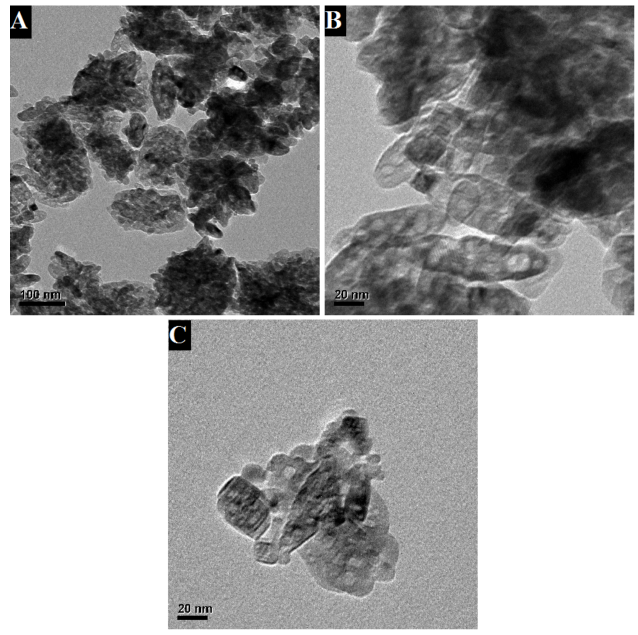

Figure 1: TEM images of 2-D brookite nanosheets.

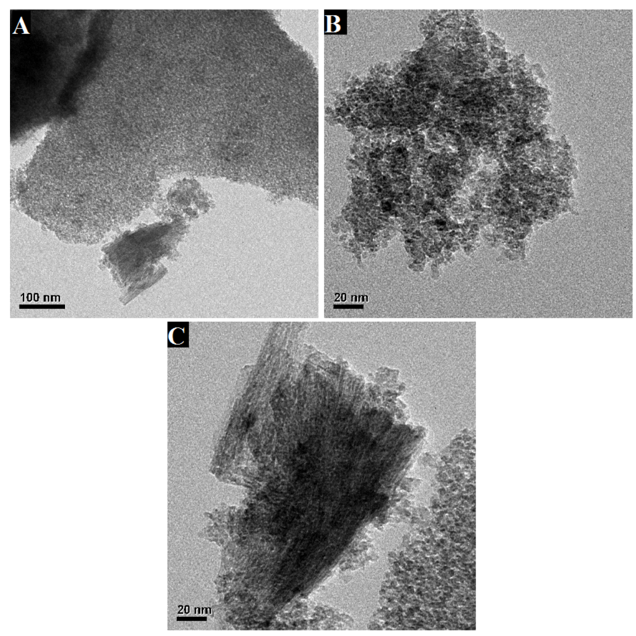

Figure 2: TEM images of rutile, showing mesoporous nanoparticle and nanoneedle microstructures.

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