Supplementary Information

Highly Pseudocapacitive Nb-doped TiO2 High Power Anodes for Lithium-ion Batteries

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Continuous Hydrothermal Flow Synthesis

Continuous hydrothermal flow synthesis (CHFS) processes are a promising route for the direct and controlled manufacture of nanomaterials. Such processes use superheated water and metal salt mixtures as reagents. In a typical CHFS reaction, a feed of supercritical water (above the critical point of water, $T_C = 374$ °C and $P_c = 22.1$ MPa), is rapidly mixed in an engineered mixer (confined jet mixer, CJM) with a metal salt/base aqueous precursor feed (at ambient temperature and the same pressure), resulting in rapid formation of the corresponding nanocrystallite oxide in the water. The general scheme of the method is presented in Figure 1.

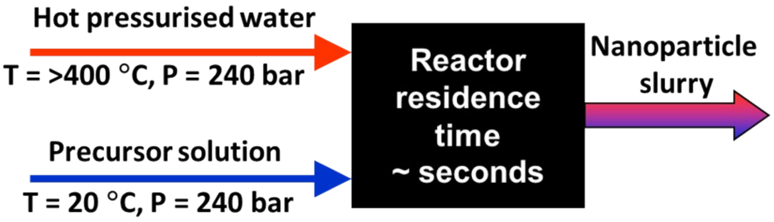

Figure 1: General scheme of the method.

In the CJM, the nucleation dominated reaction occurs as a result of the metal salts being supersaturated upon mixing with supercritical water and also instantly being hydrolyzed and dehydrated under these exotic reaction conditions. The nascent nanocrystallite metal oxide stream in water is cooled in process and can then be constantly collected from the exit of the CHFS process as aqueous nanoparticle slurry at ambient temperature. The cleaned crystallites can be obtained as a wet solid and then freeze-dried to retain maximum surface area and reduce agglomeration[1].

In Figure 2, a more detailed scheme of the process is presented. As mentioned in the experimental part, the nanoparticles were synthesized using a laboratory scale continuous hydrothermal flow synthesis (CHFS)[2-4] reactor incorporating a CJM[5, 6]. In the lab scale process (Figure 2a), three identical diaphragm pumps (Primeroyal K, Milton Roy, Pont-Saint-Pierre, France) were used to supply three feeds, which were pressurized to 24.1 MPa. Pump 1 supplied a feed of DI water at a flow rate of 80 mL min^{-1}, which was then heated above the critical point of water ($T_c = 374$°C and $P_c = 22.1$ MPa) in a flow using a 7 kW electrical water heater. Pump 2 supplied the metal salt (precursor 1) at a flow rate of 40 mL min^{-1} and pump 3 supplied either auxiliary reagents (precursor 2) or DI water at a flow rate of 40 mL min^{-1}. The feeds from pumps 2 and 3 were combined at room temperature in a dead volume tee-piece. This precursor mixture was then brought into contact with the flow of supercritical water co-currently in a CJM (Figure 2b).

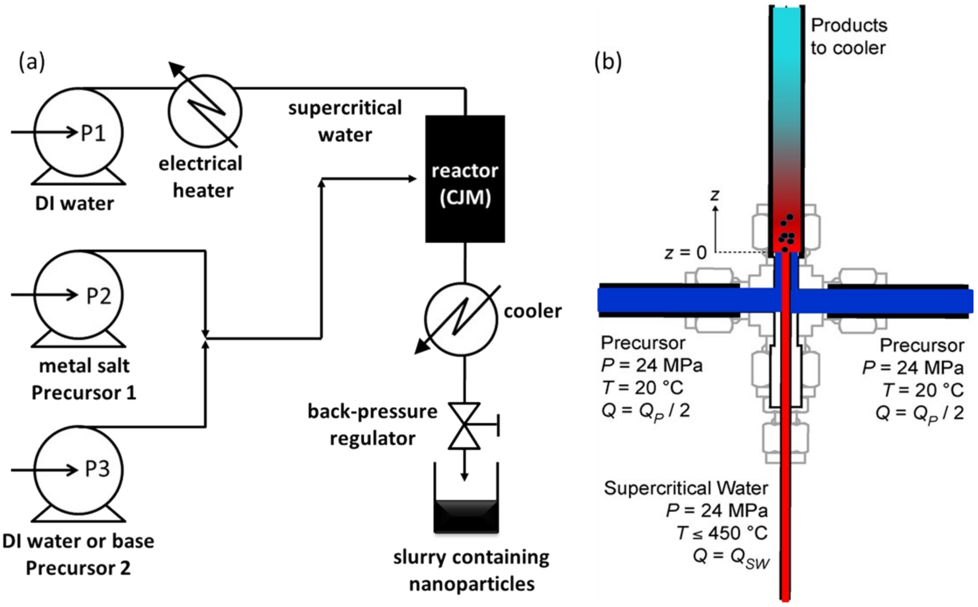

Figure 2: Scheme of the CHFS reactor (a) and the confined jet mixer (b).

XPS compositional analysis

For the estimation of elemental composition of Nb-doped TiO_2 by XPS, high resolution scans were conducted for Ti(2p) and Nb(3d) regions. Backgrounds were subtracted using the Shirley routine and peaks fitted with a Gaussian/Lorentzian line shape. Peak areas were then calculated and the concentration of Nb within the sample relative to Ti was calculated according to equation 1:

$$c_{Nb} = \left\{\frac{I_{Nb}}{S_{Nb}}\right\} / \left\{\left(\frac{I_{Nb}}{S_{Nb}}\right) + \left(\frac{I_{Ti}}{S_{Ti}}\right)\right\} \qquad (1)$$

where c_{Nb} is the concentration of Nb with respect to Ti and I_x and S_x are the peak area and atomic sensitivity factor for element x, respectively.

References

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