

Mesoporous TiO₂ anatase as negative electrode for Li-ion batteries.

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In recent years, many works focused on TiO₂ as negative electrode for Li-ion batteries. TiO₂ has various crystal types, such as anatase, rutile, brookite or TiO₂(B). The lithium insertion into these hosts has been investigated but it appears that only the anatase and nanowires TiO₂(B) forms give satisfactory electrochemical performances [1,2]. The capacity of TiO₂ anatase is about 0,6 lithium ion at 1,78V vs Li⁺/Li [3]. But its electrochemical performance depends strongly on the size and shape of particles. Indeed, too small particles are handicapped by a strong charge irreversibility due to parasitic surface reactions [4]. A few papers deal with electrochemical Li insertion into mesoporous Zr [5], Al [6] or Sn [7] modified titanium dioxide with the anatase structure. The main problem with TiO₂ is that it crystallizes easily during the calcination process destroying the mesoporous nature of the system. Here, we present some results obtained by using pure mesoporous TiO₂ anatase as positive electrode in Li//TiO₂ cells.

Mesoporous TiO₂ was prepared via a sol gel method from a modified ethylene glycol Ti precursor in presence of surfactant at pH = 2. The obtained solid was then annealed at 400°C / 4h under air. Only anatase structure was detected by XRD while the BET specific surface area was comprised between 90 and 140 m².g⁻¹ with pore diameter close to 6 nm.

The electrochemical measurements are based on cyclic voltammetry and galvanostatic technics. The voltammogram (fig 1) shows two peaks, the main at 1,7 V is usually observed for polycrystalline [8] and single crystal anatase [9]. The second at 1,5 V suggests some surface processes probably due to the presence of amorphous TiO₂.

We also focus on the capacity retention exhibited by this material when using low discharge and high charge currents. The galvanostatic curves have been recorded using a voltage window of 1,2-3,2V. The electrolyte solution is 1M LiPF₆ in EC/DMC (1/1). The mesoporous material shows unusual fast deinsertion capabilities. Only a small loss of capacity is observed by increasing charge current. Discharging capacity remains constant at about 160 mAh.g⁻¹ and charging capacity decreases from 160 to 140 mAh.g⁻¹ with charge current from C/20 to C (fig2). The capacity retention is also very good, we observe no capacity loss during the 10 first cycles (fig3) with a reversible capacity close to 140 mAh.g⁻¹. The relationships between mesoporosity and electrochemical performances will be discussed.

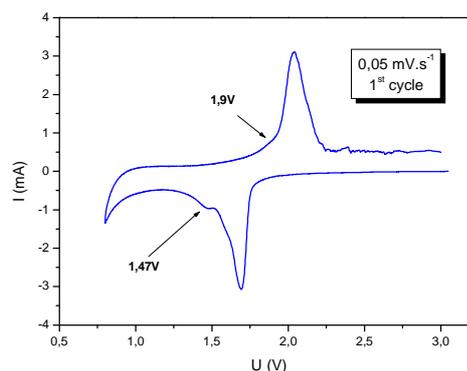


Fig 1: Cyclic voltammogram of mesoporous TiO₂ anatase in 1M LiPF₆ + EC/DMC (1/1 wt), scan rate 0,05 mV.s⁻¹

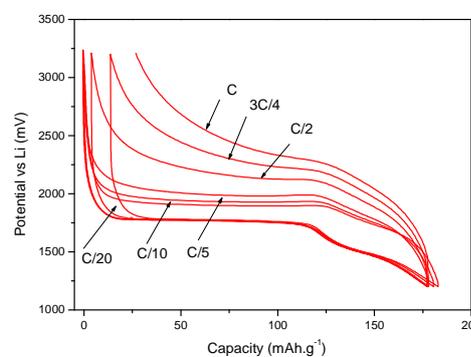


Fig 2: Galvanostatic Li⁺ insertion into mesoporous TiO₂ at constant discharge current (C/20) and different charge current.

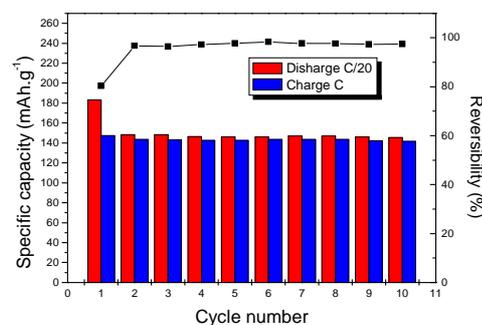


Fig 3: Capacity evolution and reversibility at low discharge current (C/20) and high charge current (C).

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