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A hydrogel template synthesis of TiO₂ nanoparticles for aluminium-ion batteries

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Abstract

Titanium dioxide nanoparticles were obtained by using poly-acrylic acid gel in a two-step synthesis method at room temperature using titanium (IV) chloride as titanium source. The formed nanoparticles were studied by different characterization techniques, showing that different proportion of anatase/rutile phase can be obtained by adjusting the amount of acrylic acid in the initial gel. Aluminum storage performance of the synthesized materials was also investigated, obtaining higher capacity density results at higher rutile ratio (75.1 mAh g⁻¹).

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1. Introduction

Rapid growth in the electrical devices market and electric vehicles, along with the necessity of energy storage obtained from renewable technologies increase the demand on electrical energy storage systems. In this regard, rechargeable batteries are considered the most viable solution to afford this demand growth due to their high efficiency.[1]

Within existing electrochemical storage batteries, rechargeable lithium-ion batteries are considered one of the most attractive due to their high energy density and low self-discharge rate.[2-4] However, these batteries work by using organic electrolytes which usually are highly toxic and with the possibility of

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causing fire hazards.[5] This risk can be avoided by replacing the organic electrolyte with an aqueous electrolyte. Several studies about aqueous metal-ion batteries have been reported,[6] focusing on the development of new electrodes with the goal to reach similar grade of efficiency as compared to the well-established Li-ion batteries. Recently research works using anatase titanium dioxide (TiO_2) have shown promising results as working electrode in aqueous Al-ion batteries. [7, 8] However, the synthesis of this material entails long complex steps as well as the utilisation of strong acids, raising the preparation costs and can limit the production at large scale. We herewith describe a new two-step synthesis protocol for the production of TiO_2 electrodes: preparation of initial titanium gel and subsequent annealing at 450 °C. Moreover, this new method allows not only the utilization of low-cost inorganic titanium sources (such as titanium chloride), but also different anatase/rutile ratios by adjusting the gel conditions. Textural/structural properties as well as its electrochemical performance in an aqueous rechargeable aluminium-ion battery were studied, showing outstanding capacity results at higher rutile/anatase ratio. This work is helpful to open up new direction of TiO_2 materials fabrication for ultra-cheap rechargeable aqueous Al-ion battery.

2. Materials and methods

2.1. Titanium dioxide nanoparticles synthesis

The synthesis of titanium dioxide nanoparticles was carry out by using titanium (IV) chloride as precursor, which is mixed with a gel agent composed by distilled water, acrylic acid (AA), and N,N'-methylene-bisacrylamide (MBA) as cross-linker. Different weight amounts of AA were used (i.e. 2 g, 5g and 10g) with MBA (0.3 g) and distilled water (9 g). Afterward, the polymerization initiator ($\text{K}_2\text{S}_2\text{O}_8$) was dropped into the solution with rapid stirring continuously for about 5 min at room temperature until the solution was solidified to a yellow gel. Subsequently, the titanium gel precursor was calcined at 450 °C for 4 h, with a ramp of 2 °C/min under an air flow to remove the organic gel and obtain the TiO_2 anatase/rutile nanoparticles powder. Different materials were named according to the amount of AA utilised: Ti2, for 2 g of AA; Ti5 for 5 g of AA; and Ti10 for 10 g of AA.

2.2. Characterization

The structural properties of the materials were characterized by X-ray diffraction using a Bruker D8 Advance diffractometer (40kV, 30 mA) with $\text{CuK}\alpha$ radiation ($\lambda=0.15418$ nm), in a 2θ range 10-80°, at a step size of 0.02° and a counting time per step of 5 s. The morphology and dispersion of titanium dioxide nanoparticles were studied by transmission electron microscopy (TEM), JEM-2100 TEM, at an operating voltage of 200 kV. Prior to the measurement, the solids were ultrasonically dispersed in acetone and dropped onto a copper grid.

2.3. Electrochemical measurements

The TiO_2 electrode was prepared following the process described in a previous study.[7] Polyvinylidene difluoride, N-methylpyrrolidone and acetylene black were purchased from Aladdin and used as received. 1 M AlCl_3 solution was prepared by dissolving AlCl_3 granules (99%, International Laboratory USA) in 18.2 M Ω deionized water (Barnstead Smart2Pure, Thermo Scientific, USA). TiO_2 sample powders (8 mg), polyvinylidene difluoride (1 mg) and acetylene black (1 mg) were dispersed in 500 μl N-methylpyrrolidone within an ultrasonic bath for 1 hour. After that, 5 μl of the result composite was dropped onto a Pt electrode with 3.0 mm diameter and then heated to 40 °C in an oven for 3 hours.

Then the electrode was covered by 30 μ l of 1% Nafion ethanol solution and then heated to 60 $^{\circ}$ C for 1 hour.

The electrochemical behaviors of TiO_2 were studied in a standard three-electrode system containing 1 M AlCl_3 solution with Pt plate electrode and a saturated silver chloride electrode (Ag/AgCl) as the counter and reference electrodes, respectively. Cyclic voltammetry (CV) measurement was performed at a scan rate of 20 mV/s between -1.5 and -0.2 V (vs. Ag/AgCl). The charge/discharge test was performed at a current rate of 0.5 A/g with a potential window of -1.25 and -0.7 V (vs. Ag/AgCl). All electrochemical measurements were conducted under room conditions using an electrochemical station CHI660E.

3. Results and discussion

3.1. Synthesis and characterization

Titanium dioxide nanoparticles were synthesized by using polyacrylic acid gel at different AA/MBA weight ratios, along with titanium chloride at room temperature. The formed titanium gel was then heated at 450 $^{\circ}$ C for 4 h to remove the organic gel and obtain the TiO_2 material. The phase composition and crystalline size of the TiO_2 produced were studied by XRD. Figure 1 represents the patterns of the synthesized titania nanoparticles. Diffractogram clearly shows the formation of anatase structures in all the synthesized materials with a nanoparticle size ca. 14-16 nm, which was calculated by Debye Scherrer's formula using the (101) peak. Besides, an incremental proportion of rutile phase is observed in Ti 5 and Ti 10, which could be related to the higher AA/MBA ratio used during the gel synthesis.

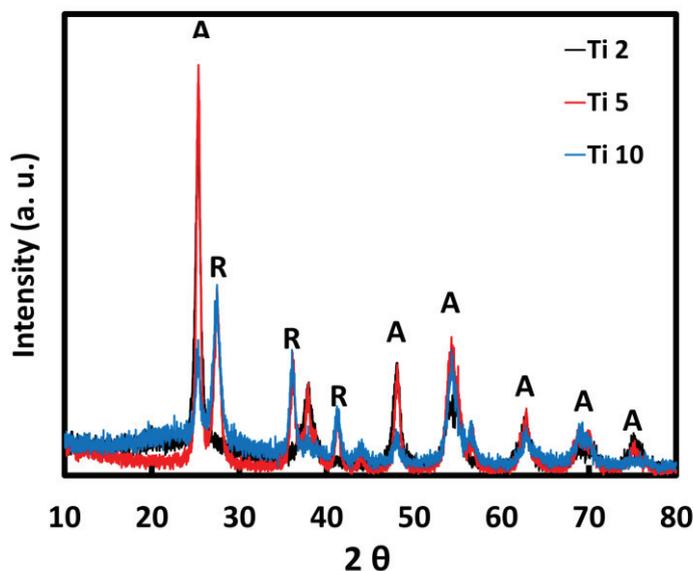


Figure 1. XRD patterns of TiO_2 nanoparticles.

TEM micrographs in Figure 2 showed a uniform spherical-like morphology of the synthesized titania nanoparticles, with an average particle size of 16 nm, which is in good agreement with the results obtained by XRD.

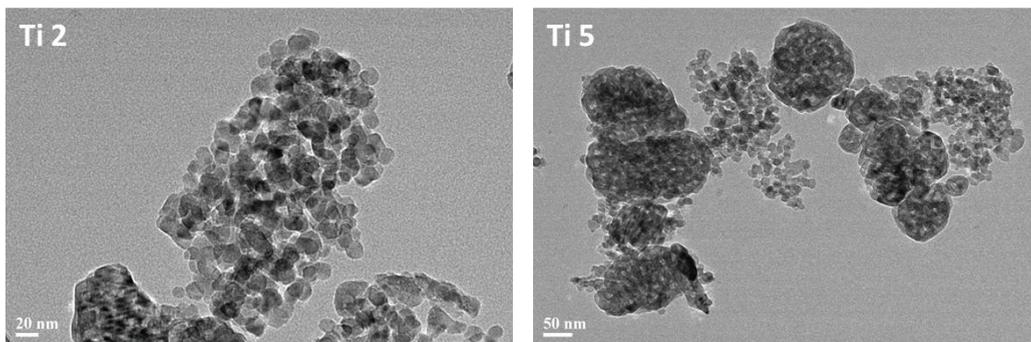


Figure 2. TEM micrographs of Ti 2 and Ti 5 materials.

3.2. Electrochemical performance

Figure 3 presents the CV curves of the three TiO₂ samples. The insertion/extraction peak potential positions are listed in Table 1. The CV tests of the three TiO₂ samples revealed that aluminum ions insertion was preferential to hydrogen evolution in aqueous solution, as a decrease of current at potential lower than -1.2 V was observed. Meanwhile, different Al³⁺ insertion/extraction performance of TiO₂ samples were presented by the CV curves. As can be observed, with the existence of rutile phase in Ti 10, the insertion and extraction currents appear on various potential positions, leading to indistinct extraction and insertion peaks. While between Ti 2 and Ti 5, Ti 5 had a smaller difference between extraction and insertion peaks. On the other hand, both the intensity and area of the peak of the Ti 2 sample were higher than Ti 5, indicating a capability of higher charge and discharge rate.

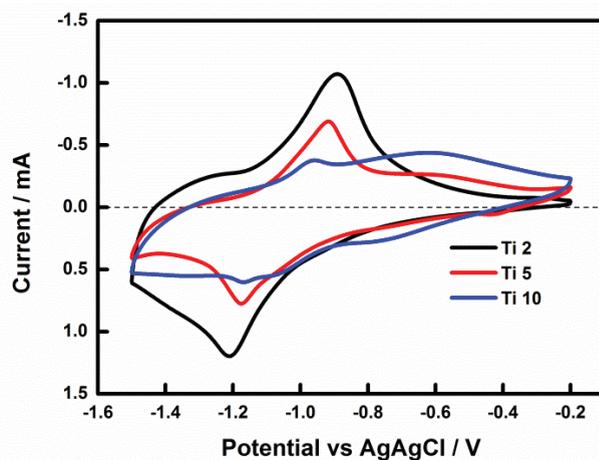
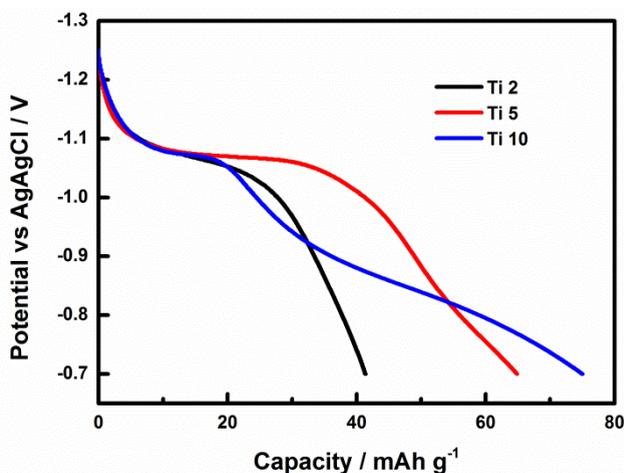


Figure 3. Cyclic voltammograms of the different TiO₂ samples (i.e. Ti2, Ti5 and Ti10).

Table 1. Extraction/insertion peak positions of the three TiO₂ sample CV curves shown in Figure 1.

	Ti 2	Ti 5	Ti 10
Extraction Peak / V vs. Ag/AgCl	-0.891	-0.917	-
Insertion Peak/ V vs. Ag/AgCl	-1.210	-1.172	-

The initial discharge curves for different TiO₂ samples at a current density of 0.5 A/g are shown in Figure 4. Similar monotonic voltage drops to around -1.08 V occurred first. After that, Ti 5 showed a largest voltage platform at around -1.05V. Ti 2 and Ti 5 were characterized with a more stable discharge platform. Among them, Ti 5 had a higher capacity density of 64.9 mAh g⁻¹, compared with 41.4 mAh g⁻¹ for Ti 2. On the other hand, Ti 10 showed a highest capacity density of 75.1 mAh g⁻¹ with another lower voltage platform around -0.85 V.

Figure 4. Discharge curves of the three kinds of TiO₂ samples (i.e. Ti 2, Ti 5 and Ti 10) at a current rate of 0.5 A/g.

4. Conclusion

Titanium dioxide nanoparticles with different anatase/rutile ratios were used as cathode materials for rechargeable aqueous aluminum-ion battery. Outstanding results on capacity density were obtained at higher rutile phase concentration, achieving the highest value of 75.1 mAh g⁻¹ by the Ti 10 sample. These initial results using a straightforward and cost-competitive synthesis method of titanium dioxide nanoparticles will help in the development of ultra-cheap rechargeable aqueous aluminium-ion batteries.

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Biography

Dr Huizhi Wang is an assistant professor at Heriot-Watt University. Her main research interest lies in electrochemistry for energy storage and carbon conversion. She has over 40 publications in peer-reviewed journals and international conferences, 3 invited book chapters and 6 patents.