



Amorphous titanium oxide passivated lithium titanium phosphate electrode for high stable aqueous lithium ion batteries with oxygen tolerance



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ABSTRACT

Undesirable side reactions at interface usually ruin the electrode stability and lead to serious self-discharge or decrease the coulombic efficiency. An ionic permeable and electronic insulating amorphous TiO₂ passivation could be deposited on the carbon encapsulated LiTi₂(PO₄)₃ electrode through sol-gel method, which drastically enhance the aqueous electrode stability and oxygen tolerance in wide potential window by kinetically suppressing the side reactions at new formed interface. Raman depth profile and SEM have confirmed this surface coating, while nanoelectronic conductivity analysis reveal the TiO₂ layer is electronically insulate. The capacity retention of the TiO₂ passivated carbon encapsulated LiTi₂(PO₄)₃/LiNO₃/LiMn₂O₄ coin cell for 2000 cycles is 66% assembled in ambient air, which is higher than 55% for the one without TiO₂ coating. Electrochemical investigation suggests the TiO₂ layer is Li⁺ ionic conductive, which suppressed the surface water reduction or oxygen reduction reaction. As an interestingly result, the cell stability improvement also benefited from the less degradation of the LiMn₂O₄ counter electrode. This comprehensive understanding of the electrode passivation using an ionic conductive layer can be potentially applied in other electrochemical devices.

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1. Introduction

As the rapid depletion of the fossil fuels is causing severe concerns on both sustainable civilization and the environmental balance, one of the most promising solutions is to develop novel energy converting and storage devices, such as solar photovoltaics [1], photoelectrochemical cells [2] and batteries [3]. Lithium ion batteries exhibit increasing applications in portable electronics, electric vehicles and smart grids [4,5]. However, they still suffer from some intrinsic problems, including the high fabricating cost, toxic flammable organic electrolyte and slow charging performance. The aqueous rechargeable lithium batteries (ARLBs) firstly developed by J. Dahn in 1994 [6], have attracted alternative attention due to their environmental friendliness, high safety and

power rate capability [7]. High performance ARLBs require reversible lithiation & delithiation reactions in the stable working window (thermodynamically less than 1.23 V) [8]. Out of this window, the side reactions, such as oxygen evolution reaction (OER), hydrogen evolution reaction (HER) and/or oxygen reduction reaction (ORR) relating to the H₂O or O₂, unavoidably deteriorates the electrode structures or the electrolyte, resulting in the cycling performance decrease, even for aqueous Li-air batteries [9]. The common strategy for increase the electrode stability is to limit the cycling potential window, leading to the energy density decrease as a tradeoff. Other novel strategies, including the protection of the electrode, the crystal structures modification and optimizing the electrolytes [10–13] become more desirable [14,15], but the electrode degradation has not well been solved in aqueous system [16].

Take lithium titanium phosphate (LiTi₂(PO₄)₃), one of the most promising anode materials (-0.55 V vs. SHE) for aqueous lithium batteries [17,18] as an example, the cell stability is extremely poor in presence of oxygen [19]. Various methods, such as carbon coating, elimination of oxygen, varying the pH or the concentration

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of the salts of the electrolyte, have been developed to improve the electrode stability. In Xia's group, Luo et al. prepared uniform carbon coated $\text{LiTi}_2(\text{PO}_4)_3$, where the $\text{LiTi}_2(\text{PO}_4)_3/\text{Li}_2\text{SO}_4/\text{LiMn}_2\text{O}_4$ cells showed good cycling stability [19]. Later, by eliminating oxygen, they found that the $\text{LiTi}_2(\text{PO}_4)_3/\text{Li}_2\text{SO}_4/\text{LiFePO}_4$ batteries exhibited excellent stability and the capacity retention over 90% after 1000 cycles [9]. Recently, Sun et al. achieved a superior cycling stability of $\text{LiTi}_2(\text{PO}_4)_3$ by high quality carbon coating [20] or nitrogen-rich doped carbon coating [21]. Huang et al. also prepared carbon coated $\text{LiTi}_2(\text{PO}_4)_3$ nanoporous microplates showing $76 \text{ mAh}\cdot\text{g}^{-1}$ at a power rate of $20 \text{ mA}\cdot\text{g}^{-1}$ [22]. It is worth noting that the stability of $\text{LiTi}_2(\text{PO}_4)_3$ can be improved by the conductive carbon encapsulation and the eliminating of oxygen [22,23]. Mostly, both strategies work consequently in a single system, which is possibly ascribed to the side reactions on the electrode have not been effectively eliminated through the electronic conductive carbon coating [9,19,24]. An important evident is the serious self-discharge of aqueous batteries with poor O_2 tolerance. There are various chemical or electrochemical reasons accounting for it: a) high operating potential window than the thermodynamic limits; b) mismatch of the electrode potential relative to the water splitting potential or c) inappropriate surface side reaction kinetics. Unfortunately, there are few protection layers for ARLBs, while it is easily formed as the solid-electrolyte interface (SEI) layer in non-aqueous batteries [25–27].

An external protection layer, either the solid electrolyte or semi-solid electrolyte, can intrinsically hinder the surface side reactions by limiting the electron transfer and enable the Li^+ ion diffusion. For instance, Wu et al. have developed a hybrid solid electrolyte for Li anode protection, which showed a wide stable operating window [14]. Recently, a “water in salts” electrolyte was reported by Suo et al., to form a SEI layer in aqueous media by use of the Li^+ -solvation sheath structure [11]. Lu et al. prepared silica nanoparticles doped aqueous electrolyte for hybrid aqueous batteries restraining the zinc dendritic crystals deposition, and reduced the self-discharge [28].

In our group, we are focusing on the protection layer to improve the cycling stability of the ARLBs. As TiO_2 has been regarded as advanced protection/passivation layers on either photoelectrodes [29–32] or battery electrodes [33,34]. Moreover, Yang et al. have successfully prepared hierarchical TiO_2 based nanobranched and nanotubes as high stable electrode materials for lithium (or sodium) ion batteries [35,36]. Herein, we used amorphous TiO_2 as passivation layer on carbon coated $\text{LiTi}_2(\text{PO}_4)_3$ electrode to reduce the surface electronic conductivity. The confocal Raman spectra and the contact angle analysis confirmed this surface coating of a- TiO_2 . Nanoelectric conductivity by the Bruker Peakforce-Tuna techniques [37,38] revealed the insulate amorphous TiO_2 layer. The cycling stability performance of the electrodes were investigated by cyclic voltammetry and battery analyzer.

2. Experimental

2.1. Materials

All the chemicals, TiO_2 , Li_2CO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, glucose ($\text{C}_6\text{H}_{12}\text{O}_6\cdot\text{H}_2\text{O}$), MnO_2 , tetrabutyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, TBOT), ethanol and ammonia were obtained from Sinopharm Chem. Reagent (China). The polyvinylidene fluoride (PVDF), N-Methyl-2-pyrrolidone (NMP), super-P carbon and the coin cell cases were used from MTI (Kejing Star, Shenzhen).

The carbon encapsulated $\text{LiTi}_2(\text{PO}_4)_3$ was prepared by the modified solid state reaction [39,40]. Briefly, the Li_2CO_3 , TiO_2 , $\text{NH}_4\text{H}_2\text{PO}_4$ and glucose (mole ratio of 1/4/6/1) were mixed by ball milling (DM-4L, Nanjing) for 2 h. The solid mixture was then heated in Ar flow (30 SCCM) from room temperature to 600°C and

maintained for 1 h, then increased to 800°C and kept for 4 h. A black $\text{LiTi}_2(\text{PO}_4)_3$ powder was obtained (in the following part, unless specified, we used $\text{LiTi}_2(\text{PO}_4)_3$ for our carbon encapsulated lithium titanium phosphate samples.). For LiMn_2O_4 preparation, the stoichiometric amounts of Li_2CO_3 and MnO_2 (1/4) were ball mixed for 2 h, before thermal annealing at $700\text{--}800^\circ\text{C}$ for 6 h in air.

2.2. Electrode preparation

The viscous slurry containing active materials, conductive carbon and PVDF (weight ratio of 7/2/1) in the certain amount of NMP was blended in agate mortar. Then the slurry was applied on a cleaned stainless steel (SS) substrate, which was dried in oven at 100°C overnight. The corresponding $\text{LiTi}_2(\text{PO}_4)_3$ and LiMn_2O_4 electrode films were then obtained.

2.3. Amorphous TiO_2 layer preparation

A TiO_2 sol was hydrolyzed from 3.3 mL of TBOT solution in ethanol ($v/v=1/10$), by slowly dropwise adding of ammonia solution (1/50 dilute by ethanol). $30 \mu\text{L}$ of the TiO_2 sol was coated on the $\text{LiTi}_2(\text{PO}_4)_3$ electrode films using a spin coater (KW-4A: 2000 rpm for 20 s). After that, the films were calcinated at $120\text{--}200^\circ\text{C}$ for 24 h, named as $\text{TiO}_2/\text{LiTi}_2(\text{PO}_4)_3$.

2.4. Characterization

The X-ray powder diffraction (XRD) was conducted on a Bruker X-ray diffractometer (D8 Advance, $\text{CuK}\alpha$, $\lambda=1.5418 \text{ \AA}$) in the range of $10\text{--}70^\circ$. The scanning electron microscopy (SEM) was observed on a field emission scanning electron microscope (Nova NanoSEM 450). HRTEM images were collected on a Tecnai G2 F20 transmission electron microscope. The Brunauer-Emmett-Teller (BET) surface area was analyzed on a Micromeritics ASAP 2020 system, using N_2 adsorption and desorption isotherms. The thermogravimetric analysis (TGA) were performed on a Netzsch thermoanalyzer (STA 449 F1 Jupiter) from room temperature to 900°C with air. Raman spectra were collected on a Renishaw confocal Raman microscope (in Via Reflex) using a green laser (532 nm) from 100 cm^{-1} to 2000 cm^{-1} . The static contact angles were recorded at ambient condition on a JC2000D2 analyzer (Shanghai Zhongchen) using static DI water drop.

The nanoelectric properties of the $\text{LiTi}_2(\text{PO}_4)_3$ and $\text{TiO}_2/\text{LiTi}_2(\text{PO}_4)_3$ films were measured using a Bruker atomic force microscopy (Dimension Icon with Peakforce Tuna) under ambient condition with a dc bias of 10 mV, using a Pt/Ir coated silicon nitride probe (Bruker PFTUNA). For the $I\text{--}V$ curve of the sample, the dc bias ramped from -40 mV to 40 mV at the same position.

In ambient air, the aqueous two-electrode cells were assembled in coin cell case (CR 2016), with a $\text{LiTi}_2(\text{PO}_4)_3$ anode, a glass fiber separator (450 nm) and a LiMn_2O_4 cathode, and 1 M LiNO_3 electrolyte ($\text{pH}=9.3$). The capacity and cycling stability of the cells were investigated on a battery analyzer (Land, CT2001A 5V1 mA, China). The cyclic voltammetry (CV) of the cells were measured on a potentiostat (CHI 660E, Shanghai) in two-electrode configuration, while the $\text{LiTi}_2(\text{PO}_4)_3$ and LiMn_2O_4 were also measured in three-electrode configuration using saturated calomel electrode (SCE) as reference electrode and a Pt wire as counter electrode. The potential (E_{RHE}) versus reversible hydrogen electrode (RHE) is converted according the equation: $E_{\text{RHE}}=E_{\text{SCE}}+0.059\text{pH}+0.241$, where E_{SCE} is the working electrode potential measured versus SCE.

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