Effect of solid electrolyte interface (SEI) film on cyclic performance of Li$_4$Ti$_5$O$_{12}$ anodes for Li ion batteries

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HIGHLIGHTS

- An SEI film can be formed on the surface of Li$_4$Ti$_5$O$_{12}$ anode even above 1 V.
- The formation of SEI film is much affected by the morphology of the electrode.
- It is assumed that the SEI film has a significant effect on cyclic performance of Li$_4$Ti$_5$O$_{12}$ electrode.
- It is found that vinylene carbonate (VC) helps rapid formation of a protective SEI film on Li$_4$Ti$_5$O$_{12}$.

ARTICLE INFO

ABSTRACT

Understanding the formation of SEI films on Li$_4$Ti$_5$O$_{12}$ (LTO) anodes offers a major benefit to large-scale applications of lithium ion batteries made therefrom. This paper reveals that an SEI film is formed above 1 V due to the interfacial reaction between the electrode and electrolyte: LTO anodes are previously considered free from SEI films when cycled between 1 and 3 V. The reactivity and the formation of SEI films are much affected by the morphology and surface area of the electrode. To study the above, LTO powders with different morphologies are synthesized using lithium acetate (LA) and lithium hydroxide (LH) as the lithium sources. LTO–LH consisting of agglomerates of primary small particles with a large surface area has higher reactivity than LTO–LA with a cubic structure and small surface area. As a result, the LTO–LH anode with a smooth SEI film offers better cyclic performance than the LTO–LA anode with a porous SEI film. The addition of vinylene carbonate to the electrolyte facilitates rapid formation of a protective SEI film on LTO–LA, greatly improving the rate and cyclic performance: stable specific capacity of 155.6 mAh g^{-1} and remarkable 135.2 mAh g^{-1} after 500 cycles at 10 C are recorded.

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1. Introduction

Spinel Li$_4$Ti$_5$O$_{12}$ (LTO) has a theoretical capacity of 175 mAh g^{-1} and exhibits excellent reversibility due to its zero volume change during charge/discharge cycles. LTO also demonstrates excellent thermal stability and cyclic performance, making it a potential anode material for high power applications [1–3]. Nevertheless, LTO suffers from a low intrinsic electronic conductivity and lithium-ion diffusion coefficient [4,5], resulting in poor high-rate capacities. Extensive studies have hitherto been carried out to address these issues and different material modifications have been proposed with varied success, including carbon coating [6–9], metal and non-metal ion doping [5,10–13], hybridization with carbon and metal powders [14–19], reduction in LTO particle size [20], etc. In addition, various nanostructured Li$_4$Ti$_5$O$_{12}$, such as hollow microspheres [21], flower-like nanosheets [22], sawtooth-like nanosheets [23], hierarchical structures [24] and rutile-TiO$_2$ nanocoatings [4], have been prepared using lithium hydroxide as the lithium source based on the hydrothermal method. They all presented high rate charge/discharge performance due to the large surface area required for reactions with the electrolyte. Nevertheless, these electrode materials often showed low tap densities and high irreversible capacity losses.

Another important reason behind the use of LTO as a potential anode material for high power lithium ion batteries (LIBs) is that LTO is considered free from SEI films and therefore is much safer and more stable than carbon-based materials. LTO

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has a stable voltage plateau at approximately 1.5 V versus Li^+/Li and its end discharge potential is usually 1 V, both of which are above the potential range where most electrolyte materials or solvents are reduced [25–27]. This means that the reduction of electrolyte on the surface of LTO can be effectively avoided due to the favorable potential difference. However, this fact is often incorrectly understood that an SEI film cannot be formed on the LTO surface.

It is well-known that a protective SEI film has to be formed to suppress the further decomposition process of electrolyte solution and protect the carbon anode. The formation mechanisms and the properties of SEI films on a carbon anode are of paramount importance in view of their influences on electrochemical and safety performance of LIBs [28,29]. Commercial LIBs, therefore, are allowed to form an SEI film on carbon anode at a low current during the initial several charge/discharge cycles. The mechanisms involved in the film formation are known to be affected by the applied voltage, current, temperature and the type of solvent used [30–33]. In addition, the reduction products of electrolyte solution − a main component of SEI films − are easily decomposed to react with the electrolyte solution at high temperatures [34]. The high thermal reactivity of the lithiated graphite anodes with the electrolyte solution means that the carbon materials used as the dominant source of anodes for current LIBs do not have high safety performance [35,36].

It is previously misunderstood that an SEI film cannot be formed on the surface of LTO electrodes when cycled above 1 V because the electrolyte solution can only be reduced below 1 V. As such, the formation of SEI films has been neglected with little attention so far. However, we demonstrated in this study that an SEI film could also be formed on the surface of LTO electrodes when cycled at 1–3 V. The interfacial reaction between LTO and the electrolyte solution was responsible for the observation, greatly affected by the morphology of LTO powders. The formation mechanisms and the role of the SEI films during the cyclic tests were successfully identified. Particular emphasis was placed on evaluating the effects of SEI films on the rate and cyclic performance of LTO electrodes. For this purpose, a facile hydrothermal method was employed to prepare LTO particles using cetyltrimethylammonium bromide (CTAB) as a surfactant to control the hydrolysis rate of tetrabutyl titanate ($Ti(OC_4H_9)_4$). To specifically evaluate the reactivity and the formation of SEI films, LTO powders with different morphologies were prepared using lithium acetate (LA) and lithium hydroxide (LH) as the lithium source.

2. Experimental

2.1. Synthesis of LTO–LA and LTO–LH

CTAB was used as a surfactant in the hydrolysis process. 0.39 g CTAB was dissolved into 20 mL deionized water at room temperature, and 5 mL $Ti(OC_4H_9)_4$ was introduced stepwisely into the CTAB solution under magnetic stirring for 3 h to obtain a turbid liquid. It was observed that the $Ti(OC_4H_9)_4$ drop was instantly surrounded by CTA^+ cations, which in turn reduced the contact between $Ti(OC_4H_9)_4$ and water to effectively control the hydrolysis rate before forming $Ti(OH)_4$. 1.259 g lithium acetate dihydrate ($CH_3COOLi·2H_2O$) was dissolved in 10 mL purified water and the lithium acetate solution was added to the above suspension. The mixture was transferred to a 60 mL Teflon-lined stainless steel autoclave and maintained at 180 °C for 24 h. White precipitate was obtained after the hydrothermal treatment. After drying in an oven at 85 °C, the as-prepared product was calcined at 700 °C for 7 h in air to obtain LTO powders, which are designated as LTO–LA. For

comparison, LTO–LH was also prepared using the other lithium source.

2.2. Characterization of structure and morphology of LTO powders

The phase structure of the LTO powders were characterized by X-ray diffraction measurement (XRD, Rigaku D/max 2500/PC using CuKα radiation with $\lambda = 1.5418$ Å). Their morphologies were examined on a field emission scanning electron microscope (FE-SEM, HITACH S4800) at 10 kV and a field emission transmission electron microscope (FE-TEM, JEOL 2010F) at an accelerating voltage of 200 kV. Nitrogen adsorption/desorption isotherms were obtained at 77 K using an automated adsorption apparatus (Micromerit-ics ASAP 2020). The surface area was calculated based on the Brunauer−Emmett−Teller (BET) equation.

2.3. Electrochemical characterization

CR2032-type coin cells were assembled to evaluate the electrochemical performance and SEI film formation on the surface of LTO electrodes. The coin cells consisted of LTO powders as the cathode material, lithium foil as the anode, and polypropylene (Celgard 2500, Celgard Inc., USA) as the separator. The cathode consisted of 80 wt.% LTO, 10 wt.% Super-P carbon black and 10 wt.% poly(vinylidene fluoride) (PVDF) binder to form an active material of about 3.5 mg cm^{-2} with a thickness of about 45 μm, excluding the copper current collector. 1 M $LiPF_6$ in a mixture of ethylene carbonate, dimethyl carbonate and ethylmethyl carbonate (volume ratio: 1:1:1) (1 M $LiPF_6$/EC + DMC + EMC, supplied by Guangzhou Tinci Materials Technology Co. with a moisture content 4.4 ppm and an HF content 15.8 ppm) was used as the electrolyte solution. The cells were assembled in a glove box (Mbraum) filled with high purity argon gas. The assembled cells were cycled at different charge/discharge rates between 0–3 or 1–3 V (Land 2001A Battery Testing System) at room temperature. The cyclic voltammograms (CVs) of LTO electrodes were obtained on an electrochemical working station of VMP3 (Bio Logic Science Instruments) at a scanning rate of 0.1 mV s^{-1} using the LTO electrode as the working electrode, and the lithium foil both as the reference and counter electrodes. The corresponding electrochemical impedance spectra (EIS) were obtained using an electric IM6ex impedance analyzer at a frequency range of $10^{-2} \sim 10^5$ Hz and at a half state of charge by applying a 5 mV ac oscillation.

The coin cells after designated cyclic tests were fully charged before they were disassembled in the glove box for examination. The LTO electrode was rinsed using dimethyl carbonate (DMC) to remove the electrolyte from the electrode surface, and was dried to remove the residual DMC. The surface morphology of the electrode was examined on FE-SEM and FE-TEM, and their elemental compositions were analyzed using X-ray photoelectron spectroscopy (XPS, VGMicro Tech). The C 1s peak for the graphitic carbon at 285 eV was used as a reference for the calibration of XPS peaks. Fourier transform infrared spectroscopy (FTIR, Bio-rad FTS 6000) was used to evaluate the structure of SEI films in the near infrared (NIR) region (600–2000 cm^{-1}).

3. Results and discussion

The XRD patterns of both LTO–LA and LTO–LH powders were in good agreement with the JCPDS standard (card No. 49-0207) and can be indexed to the spinel structure of LTO with the space group $Fd3m$ (Fig. 1a). Weak diffraction peaks of rutile TiO_2 were detected in LTO–LH, indicating an existence of small fraction of rutile TiO_2 surface layer (see Fig. S1), which was shown to improve the rate performance of LTO [4]. LTO powders prepared using