Journal of Power Sources 388 (2018) 65–70

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Surface-protected $LiCoO_2$ with ultrathin solid oxide electrolyte film for high-voltage lithium ion batteries and lithium polymer batteries

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HIGHLIGHTS

- A continuous and compact 20 nm $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ (LATP) layer is coated on $LiCoO_2$.
- The LATP coated $LiCoO_2$ show much improved cyclic performance at 4.5 V
- Coated sample can operate in a PEO-based all-solid lithium polymer battery.

ARTICLE INFO

Keywords:
$LiCoO_2$
Surface modification
Solid electrolyte
Poly(ethylene oxide)
Solid-state battery

ABSTRACT

Surface modification of $LiCoO_2$ with the ultrathin film of solid state electrolyte of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ (LATP) has been realized by a new and facile solution-based method. The coated $LiCoO_2$ reveals enhanced structural and electrochemical stability at high voltage (4.5 V *vs* Li^+/Li) in half-cell with liquid electrolyte. Transmission electron microscopy (TEM) images show that a dense LATP coating layer is covered on the surface of $LiCoO_2$ uniformly with thickness of less than 20 nm. The LATP coating layer is proven to be able to prevent the direct contact between the cathode and the electrolyte effectively and thus to suppress the side reactions of liquid electrolyte with $LiCoO_2$ surface at high charging voltage. As a result, dissolution of Co^{3+} has been largely suppressed over prolonged cycling as indicated by the X-ray photoelectron spectroscopy (XPS) measurements. Due to this surface passivating feature, the electrochemical performance of 0.5 wt% LATP modified $LiCoO_2$ has also been evaluated in an all solid lithium battery with poly(ethylene oxide)-based polymer electrolyte. The cell exhibits 93% discharge capacity retention of the initial discharge capacity after 50 cycles at the charging cut-off voltage of 4.2 V, suggesting that the LATP coating layer is effective to suppress the oxidation of PEO at high voltage.

1. Introduction

Lithium ion batteries have promoted the revolution of portable electronic devices, as they offer high volumetric energy densities and exhibit long life cycles [1,2]. Although they can meet the demands for many consumer electronics, new applications, such as 5G mobile terminals, require higher energy and power densities. $LiCoO_2$, first discovered by *Mizushima, Goodenough* et al. [3], dominates the cathode electrode material of commercial lithium ion batteries for consumer electronics due to its high volumetric energy density as well as good rate capability and cycling stability [4]. The working voltage of practical battery based on $LiCoO_2$ is confined within ~4.45 V (vs Li^+/Li). Increasing the charging cut-off voltage of $LiCoO_2$ can significantly increase the energy densities (Table 1) [5–12]. However, for batteries using non-aqueous liquid electrolyte, side reactions between the cathode and the electrolyte lead to rapid deterioration of structural and electrochemical stability [13–15], manifested as dissolution of the transition metal ions (Co^{3+}) and sharp attenuation of discharge capacity [16–18].

All-solid lithium batteries (ASLB) have attracted wide attention. PEO-based ASLB batteries have been used in electrical vehicles [19–22]. However, PEO-based polymer solid electrolyte is not stable to

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https://doi.org/10.1016/j.jpowsour.2018.03.076
Received 11 February 2018; Received in revised form 23 March 2018; Accepted 28 March 2018

Table 1
Energy density of $LiCoO_2$ at different cut-off voltage.

Voltage(vs Li^+/Li)	4.2 V [5]	4.3 V [6,7]	4.4 V [8]	4.5 V [9,10]	4.6 V [11,12]
Capacity(mAh/g)	140	155	170	185	220
Average Voltage (V)	3.91	3.92	3.94	3.97	4.03
Specific energy (Wh/kg)	547.3	607.6	669.6	733.5	885.9
Specific energy (Wh/L)	2299	2552	2812	3081	3721
Increasing ratio[a]		11%	10%	9.5%	21%

[a] Increasing ratio of energy density.

operate above 4.0 V [23], which limits the energy density and affects it wide applications. Exploring polymer solid electrolyte with high electrochemical oxidation stability or decreasing the oxidation reactivity of the cathode in ASLB is highly desirable.

Therefore, it is critical to enhance the structural and electrochemical stability of $LiCoO_2$ and restrain its strong surface oxidation property at high voltage. Surface modification has been confirmed as an effective method [8,24–28]. Coating carbon has been proved by *Cao* et al. [27] to lower charge transfer resistance and enhance rate capacity of $LiCoO_2$. However, uniform and dense carbon coating is not easy on layered oxide compounds [28]. Coating metal oxides (i.e. Al_2O_3 [8,24–32], ZrO [33], MgO [34–37], $AlPO_4$ [38,41], etc.), first reported by *Cho* et al. [8,25,38–42], considerably enhances the capacity retention and structural stability of $LiCoO_2$. Nevertheless, most metal oxides are not lithium ion conductors, which may result in high interfacial resistance between the cathode and electrolyte. In this regard, surface modification with a lithium ion conductor has its unique advantages. Among various lithium ion conductors, NASICON-type $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) solid electrolyte, exhibiting high ionic conductivity and low cost, has attracted a lot of attention. *Morimoto* et al. [43] reported the preparation of LATP and $LiCoO_2$ composite by mechanical milling method. Although the large particles of LATP were only scattered on the surface of $LiCoO_2$ particles rather than forming a continuous layer, the composite exhibited high capacity (around 180 mAh/g) and good cycle performance at high potential (4.5 V). *Lee* et al. [44] prepared the LATP modified $LiCoO_2$ powder by a precursor coating method, and the excellent electrochemical performances in terms of the good cycling properties and C-rate capability were achieved at 4.5 V. However, elevated temperature treatment (above 500 °C) leads to the formation of passivation layer between $LiCoO_2$ and LATP [45].

Here, we report the synthesis of high-performance $LiCoO_2$ coated with continuous and compact ultrathin film of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$, through a solution-based new method followed by low temperature heat treatment. The surface properties of LATP modified $LiCoO_2$ were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The cycling performances of the LATP modified $LiCoO_2$ were evaluated in half-cell with liquid electrolyte and lithium battery with PEO based polymer electrolyte.

2. Experimental

$LiCoO_2$ and LATP were synthesized by a solid-state synthesis method. For $LiCoO_2$ powder, stoichiometric amounts of lithium hydroxide and cobalt acetate were mixed thoroughly and then heated at 400 °C for 6 h followed by 800 °C for 10 h in air [46]. For LATP powder, a stoichiometric mixture of Li_2CO_3 (99%), Al_2O_3 (98.5%), TiO_2 (99%) and $NH_4H_2PO_4$ (99.9%) precursors was ground by ball milling with a rotation speed of 300 rpm at room temperature for 5 h and heated at 400 °C for 2 h followed by 900 °C for 5 h in air [47]. The as-prepared LATP powder was fine ground by a pulverizer (VGREEN, China) to reduce the particle size and then dispersed into deionized water to form an aqueous sol. Surface modified $LiCoO_2$ was prepared by a solution-based synthesis method. $LiCoO_2$ particles was introduced into LATP aqueous sol with the loading of 0.2 wt%, 0.5 wt%, 1 wt%, 1.5 wt% (LATP to $LiCoO_2$) respectively. The slurry was stirred at 100 °C to evaporate the water, and further heat-treatment was conducted at 350 °C for 5 h to obtain the final product.

2032-type-coin-cells were assembled to evaluate the electrochemical performances of the surface-modified $LiCoO_2$, with lithium metal as the anode and 1 M $LiPF_6$ in ethylene carbonate/dimethly carbonate (EC/DMC) (1:1 vol%) as the electrolyte [32]. The cathode electrode was prepared by mixing the $LiCoO_2$ powder, carbon black and polyvinylidene fluoride (PVDF) binder with a weight ratio of 95:2:3 and blade coating on Al foil. The half-cells were charged and discharged in the voltage range of 3.0–4.5 V (*vs* Li^+/Li) with a current density of 0.2C rate (0.3 mA/g) at room temperature. Rate performance of 0.5% LATP modified-$LiCoO_2$ at 0.1C 0.2C, 0.5C, 1C, 2C and 5C was also conducted.

Polyethylene oxide (PEO) and lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) were dissolved in acetonitrile (EO/Li = 15 by mole ratio), and stirred for 5 h. The solution was casted into a Teflon dish. After drying at 45 °C for 24 h under high vacuum condition, the PEO electrolyte was obtained. The cathode electrode for polymer battery was prepared by mixing active material (modified-$LiCoO_2$ or bare $LiCoO_2$), carbon nanotube, PEO and LiTFSI with a weight ratio of 85:2:12:1 and blade coating on Al foil. Cycling performance for PEO-based batteries were evaluated at 60 °C with the cut-off potential range from 3.0 to 4.2 V and a current density of 0.2C rate.

The morphology of the modified-$LiCoO_2$ was investigated by scanning electron microscope (SEM) and transmission electron microscope (TEM). Dissolution of the transition metal (Co^{3+}) was analyzed by X-ray photoelectron spectroscopy (XPS). The XPS spectra were recorded by ESCALAB 250 Xi, Thermo Fisher with monochromatic 150 W Al Kα radiation. The data was analyzed with program Advantage and the binding energies were referenced to the C1s line at 284.4 eV from adventitious carbon.

3. Results and discussion

Inset of Fig. 1a shows the LATP aqueous sol. The nano-sized LATP, prepared by solid-state synthesis and fine ground methods, was well dispersed into the water-based solvent. The well-dispersed LATP water solution can be confirmed by the distinct Tyndall effect (Fig. 1a). Fig. S1 shows the XRD patterns of the purchased $LiCoO_2$ (Fig. S1a) and the as-prepared pure phase $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ powder (Fig. S1b). The SEM images of the surface-modified $LiCoO_2$, with LATP loading of 0 wt%, 0.2 wt%, 0.5 wt%, 1 wt%, 1.5 wt% are shown in Fig. 1b to f, respectively. The LATP modified $LiCoO_2$ powders show relatively rough surface with dot-like nano-sized particles embedded into the $LiCoO_2$ surface. These nano-sized particles are LATP which can be confirmed by EDS mapping as shown in Fig. S2. With the increase of the loading amount of the LATP, the surface coverage increases and a uniform and relatively dense membrane-like coating layer can be formed when the content of LATP exceeds 0.5 wt%.

In order to evaluate the effects of LATP coating on the electrochemical performances of $LiCoO_2$, charge and discharge measurements were performed in half-cells and the cycling performances of surface-modified $LiCoO_2$ with different loading amount of LATP are shown in Fig. 2a. All the cells were tested at room temperature with the charging cut-off potential of 4.5 V and current density of 0.2 C rate (0.3 mA/g). The LATP modified-$LiCoO_2$ exhibit excellent electrochemical stability with the discharge capacity retention of 87.6%, 93.1%, 91.8% and 87.4% after 50 cycles for the cathode with the LATP loading of 0.2 wt%, 0.5 wt%, 1 wt% and 1.5 wt%, respectively. For the small amount of LATP coating of 0.2 wt% and 0.5 wt%, it does not compromise the capacity compared to the bare $LiCoO_2$ (176 mAh/g) and the initial