



Modified electrochemical performance of high potential cathode using a sand-like carbonate electrolyte



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ABSTRACT

The electrochemical performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is investigated in a sand-like carbonate electrolyte containing 4 wt.% lithium metasilicate (Li_2SiO_3). The capacity fading rate of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode working in the sand-like electrolyte (2–5 V) is reduced to 0.171 mAh g^{-1} per cycle, quite smaller than the value of 0.613 mAh g^{-1} per cycle in the electrolyte without Li_2SiO_3 . The capacity of 159.5 mAh g^{-1} is delivered at 0.5 C after 118 cycles while it is only 99.4 mAh g^{-1} for the Li_2SiO_3 -free counterpart. Cyclic voltammetry, scanning electron microscope, X-ray diffraction, X-ray photoelectron spectroscopic measurements are conducted to explore the modification mechanism. It is found that the anodic stability of the sand-like electrolyte is improved compared to the base electrolyte. The Li_2SiO_3 precipitates on the electrode surface make contribution to the performance enhancement of the cathode at high potential.

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1. Introduction

Till now the most successful high-potential cathode materials are those based on spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO). [1] The work relevant to 5 V cathodes currently focuses on the issue of capacity fading during cycling under high cutoff potential. It has been proposed that the Jahn-Teller distortion happened near 2.7 V, the Mn dissolution and the carbonate electrolyte instability at high potential are the main reasons leading to the capacity fading. [2–4] The structure transition from cubic phase to tetragonal one near 2.7 V causes severe volume change, leading to the Jahn-Teller distortion. Mn dissolution is usually accelerated by the hydrofluoric acid (HF) generated due to the thermal/chemical instability of LiPF_6 electrolyte ($\text{LiPF}_6 \rightarrow \text{LiF} + \text{PF}_5$, $\text{H}_2\text{O} + \text{PF}_5 \rightarrow \text{OPF}_3 + 2\text{HF}$). Moreover, the generation of lewis acid PF_5 can initiate the polymerization of cyclic carbonate, degrading the electrolyte and the performance of LIBs [5–7]. In addition, electrolyte decomposition is severe at high potential due to the electrochemical instability of the carbonate electrolyte.

In general, the modification on material [8,9] and electrolyte [10–13] is effective to enhance the cycling stability of the cathode. Lithium metasilicate (Li_2SiO_3) is an alkaline inorganic lithium salt. It may interact with Lewis acid. Its superior electrochemical stability may protect the electrolyte from oxidation if it precipitates on the cathode surface. As an electrolyte additive, the effect of Li_2SiO_3 on the cycling performance of the LNMO cathode is investigated in this work. Its suppressing ability to the reactions of the electrolyte under high potential is examined as well.

2. Experimental

2.1. Preparation of electrolyte, electrode and cell

Lithium hexafluorophosphate (LiPF_6), ethylene carbonate (EC), propylene carbonate (PC) and diethyl carbonate (DEC) (Xianghe kunlun chemical products Co., LTD, China) were used without further purification. 1 mol L^{-1} LiPF_6 -EC/PC/DEC (1/1/3, wt.) base electrolyte was prepared in an Ar-filled glove box. The moisture content of the electrolyte is 33.4 ppm according to the measurement using Kari-Fisher Coulometric Moisture Meter (C20/C30), the HF content is estimated as 139.8 ppm through acid base (NaOH) titration method. Li_2SiO_3 (99.9%) were purchased from Aladdin Chemistry Co. Ltd, China, almost insoluble in carbonate electrolyte. The 4 wt.% Li_2SiO_3 -added electrolyte is a homogeneous sand-like suspension compared to the transparent solution of the base

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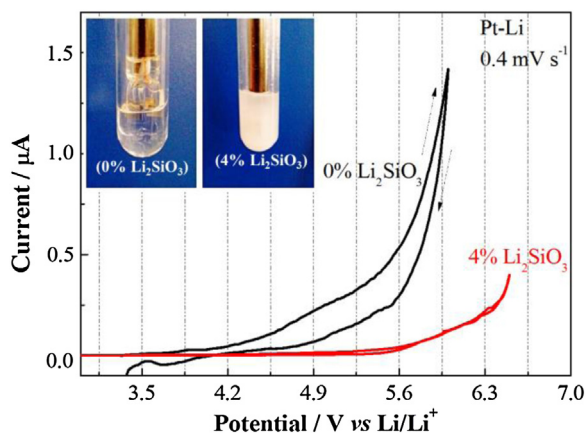


Fig. 1. CV curves of the base electrolyte (0% Li_2SiO_3) and sand-like electrolyte (4% Li_2SiO_3) on Pt electrode, the inset is electrolyte images.

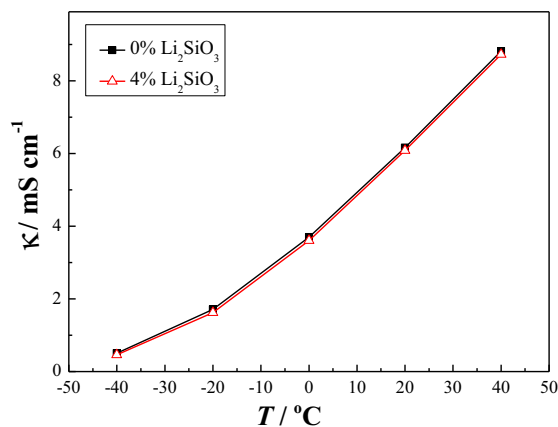


Fig. 2. The relationships between conductivities and temperatures of electrolytes.

electrolyte, as shown in Fig. 1, the amount of Li_2SiO_3 soluble in the base electrolyte is about 0.1%(wt.).

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material was got from Institute of Nuclear & New Energy Technology in Tsinghua University of China. The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li CR2025}$ coin cells were assembled with the cathode (11 mm in diameter) containing 10wt% super P, and 10wt% polyvinylidene fluoride (PVDF). Celgard 2400 polyethylene membrane was used as separator. In electrolyte changing experiment, the cell that had been cycled in 0% (or 4%) Li_2SiO_3 electrolyte for three times was disassembled in Ar-filled glove box, the cycled cathode and lithium sheet anode were washed with DEC, then reassembled using 4% (or 0%) Li_2SiO_3 electrolyte and a new separator to construct a new cell for subsequent cycling. The potential mentioned in the text was referred to the redox couple of Li^+/Li .

2.2. Characterization and Electrochemical measurements

Charge/discharge tests were carried out on CT2001A Land tester (Wuhan Jinnuo Electronics Co., Ltd.). The oxidation potential of the electrolyte was measured adopting cyclic voltammetry (CV) method on CHI660c electrochemical station (Shanghai Chenhua Co. Ltd), a Pt micro disc electrode (0.39 mm^2) was used as working electrode with lithium metal sheet as counter electrode. The conductivity of the electrolyte was tested using a conductivity meter (DDSJ-308A) through A.C. impedance method.

High resolution transmission electron microscope (HRTEM, JEM-2100), Scanning Electron Microscope (SEM, FEI, Quanta 200f) coupled with INCA energy-dispersive X-ray spectroscopy (EDX) were employed to analyze the electrode in lithiated state. X-ray photoelectron spectroscopic (XPS) measurement was performed on a PHI QUANTERA-II SXM system (Japan/Uivac-PHI, INC) with X-ray power- $\text{AlK}\alpha$ 1486.6 eV, pass energy 26.0 eV, chamber pressure $2.0 \times 10^{-7} \text{ Pa}$, take off angle 45° . The electrodes in SEM and XPS measurements were used without any solvent washing to keep the original status. The depth information of the electrolyte/electrode interphase was obtained by Ar ion beam sputtering (2 keV). The ratio of Mn to Ni was calculated based on the equation $(A_{\text{Mn}}/S_{\text{Mn}})/(A_{\text{Ni}}/S_{\text{Ni}})$, where A is the peak area of the related element and S is the corrected sensitivity number of the element acquired from the PHI QUANTERA-II SXM system. X-ray diffraction (XRD) was carried out using X-ray diffractometer with a $\text{Cu K}\alpha$ radiation source from 10° to 90° at a scan rate of 8° min^{-1} .

3. Results and discussion

As shown by CV curves in Fig. 1, oxidation current is obviously detectable at the potential higher than 4.9V for the base electrolyte ($\text{LiPF}_6/\text{EC}/\text{PC}/\text{DEC}$ with 0% Li_2SiO_3). When 4% Li_2SiO_3 is added into the electrolyte, the current doesn't appear until the potential increases to 5.6V. It is indicated that the anodic stability of $\text{LiPF}_6/\text{EC}/\text{PC}/\text{DEC}$ electrolyte is improved in the presence of Li_2SiO_3 . Meanwhile, the improvement doesn't come at the cost of sacrificing the conductivity of the electrolyte, as shown by the almost overlapped conductivity curves for the two cases in Fig. 2, irrespective of the ambient temperature. Alternatively, the Li_2SiO_3 sand-like electrolyte was applied to modify the electrochemical performance of 5V $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode.

EIS measurement employing two-electrode system was conducted to make a qualitative comparison between the cells with and without Li_2SiO_3 addition. The inset in Fig. 3 shows that the resistances of SEI film (R_{SEI}) after 3 cycles are almost the same for the two samples according to the diameter of the first semi-circle. While, it is clear that the R_{SEI} then differs remarkably from each other after 60 cycles. In the base electrolyte, the R_{SEI} enlarges nearly 4 times to 173Ω . The increased impedance is associated with a thick and resistive SEI film formed during the cycling because of the successive electrolyte decomposition [14,15]. The thick film would hamper the transport of lithium ion across the interphase. Upon using the sand-like electrolyte, the electrode shows almost no R_{SEI} increase from the 3rd to the 60th cycle with a value of about 35Ω . So, it is thought only few side reactions happen in the LNMO/Li cell

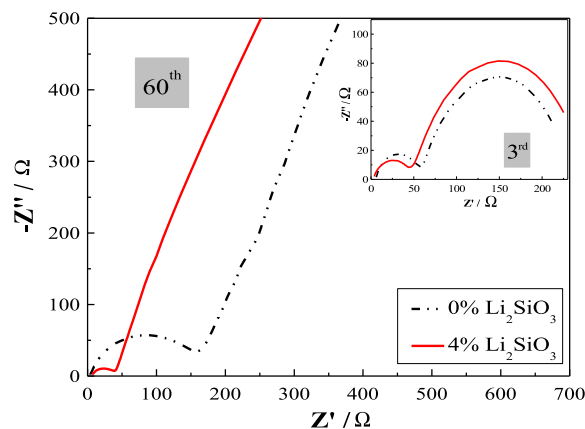


Fig. 3. EIS plots of LNMO electrode at open circuit potential (2.8V) after discharged in the electrolyte with 0% and 4% Li_2SiO_3 for 60 cycles (inset data are tested after 3 cycles).

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