



Tris(trimethylsilyl)phosphate as electrolyte additive for self-discharge suppression of layered nickel cobalt manganese oxide



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ABSTRACT

Application of layered nickel cobalt manganese oxide as cathode under higher potential than conventional 4.2 V yields a significant improvement in energy density of lithium ion battery. However, the cathode fully charged under high potential suffers serious self-discharge, in which the interaction between the cathode and electrolyte proceeds without potential limitation. In this work, we use tris (trimethylsilyl)phosphate (TMSP) as an electrolyte additive to solve this problem. A representative layered nickel cobalt manganese oxide, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, is considered. The effect of TMSP on self-discharge behavior of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is evaluated by physical and electrochemical methods. It is found that the self-discharge of charged $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ can be suppressed significantly by using TMSP. TMSP is oxidized preferentially in comparison with the standard electrolyte during initial charging process forming a protective cathode interface film, which avoids the interaction between cathode and electrolyte at any potential and thus prevents electrolyte decomposition and protects $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ from structure destruction.

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1. Introduction

Lithium ion battery is believed to be the most competitive power source for large-scale applications, but its energy density needs to be enhanced further [1,2]. One of the strategies to improve the energy density of lithium ion battery is to apply new cathode materials with high working potentials [3–6]. Among various cathode materials, layered nickel cobalt and manganese oxide, $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM, $0 \leq x, y, z < 1$), has received much attention, because its specific capacity can be enhanced when it is used under high working potential [7–12]. The energy density of a lithium ion battery based on NCM cathode can be enhanced by 30% when the end-off charge potential is increased from 4.2 V to 4.5 V due to the oxidation of Co^{3+} to Co^{4+} . The electrochemical behavior of NCM cathode involves typical Faradaic reaction in a battery, which is

distinct from that of pseudocapacitive electrode in a supercapacitor [13,14].

Nevertheless, we are facing new issues when we increase the end-off charge potential of NCM cathode. The problem we are most concerned is the failure resulting from the crystal destruction of NCM and the decomposition of electrolyte when NCM is performed with charge/discharge cycling under high potential [15–18]. Besides, NCM experiences a serious self-discharge when it is stored after fully charging at high potential, which also results from the crystal destruction of NCM and the decomposition of electrolyte [19]. The final results are the same but the involved mechanisms are different between charge/discharge cycling and self-discharge. The crystal destruction of NCM and the decomposition of electrolyte take place at high charge potential in the case of charge/discharge cycling, but proceed without any potential limitation through spontaneous interaction between charged NCM and electrolyte for the self-discharge. The former depends mainly on the thermodynamic stability of electrolyte [20,21], while the latter is related to the products from the interaction between charged cathode and electrolyte [22,23]. For example, the liberation of protons due to the interaction between charged

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NCM and electrolyte leads to the corrosion of aluminum current collector [19,24]. Therefore, it is more challenging to fight the failure resulting from self-discharge than that from charge/discharge cycling.

Motivated by the protection of solid electrolyte interface (SEI) film on graphite anode, researchers have successfully used electrolyte additives to improve cyclic stability of high potential cathode materials, which are based on the cathode interface film formed by electrolyte additives for suppressing the electrolyte decomposition and protecting cathode materials from structural destruction [25,26]. It is reasonable to infer that the cathode interface film is applicable for suppressing the self-discharge of the charged cathode under high potential. In fact, succinic anhydride [27] and tris(trimethylsilyl)borate [23] have been reported to be effective for suppressing the self-discharge of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

In our previous report, we used tris(trimethylsilyl)phosphate (TMSP) to improve cyclic stability of high potential NCM-based lithium ion battery and obtained a satisfying improvement [28]. This improvement was identified as the contribution of the cathode interface film formed from the preferential oxidation of TMSP in comparison with the standard electrolyte. In this work, TMSP was used as an electrolyte additive to suppress the self-discharge of charged NCM under 4.5 V. A representative layered nickel cobalt manganese oxide, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, is considered. The effect of TMSP on self-discharge behavior of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is evaluated by physical and electrochemical methods.

2. Experimental

2.1. Electrode and electrolyte preparation

$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode was prepared by coating a mixture of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (Qingdao Xinzheng Co. Ltd, China, 80 wt. %), acetylene carbon black (10 wt. %), and polyvinylidene fluoride (PVdF, 10 wt. %) onto an Al current collector. 2025-type coin cells were assembled with Celgard 2400 separators, electrolyte, lithium foil anode, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode in Ar-filled glove-box, where the contents of moisture and oxygen were controlled to less than 0.1 ppm and 10 ppm, respectively. Battery-grade solvents (EC, DMC) and salt (LiPF_6) were provided by Guangzhou Tinci Materials Technology Co. Ltd., China. TMSP was purchased from Fujian Chuangxin Technology Co., Ltd., China (> 99.5%) and used without further purification. The contents of HF and water in solvents and LiPF_6 were less than 5 ppm. The electrolytes used were 1.0 mol L^{-1} LiPF_6 in EC/DMC (1:2, in weight) without (standard) and with TMSP (1 wt. %).

2.2. Electrochemical measurements

Self-discharges of charged $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ were measured according to the following protocols: $\text{Li}/\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ coin cells were charged and discharged at C/5 ($1\text{C} = 160 \text{ mA g}^{-1}$) for three cycles in the potential range of 3.0–4.5 V and then left at open-circuit potential for 20 days. The cycling performance of $\text{Li}/\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ coin cells after self-discharge were tested at C/2 rate on LAND test system (Land CT2001A, China) at 25 °C. Chronoamperometry (CA) was performed on Solartron-1480 (England). Electrochemical impedance spectra were obtained on electrochemical station (Metrohm Autolab PGSTAT302N, the Netherlands) in a frequency range of 10^5 – 10^{-2} Hz with potential amplitude of 5 mV.

2.3. Physical characterizations

The cycled $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrodes for physical characterizations were rinsed with DMC three times and dried overnight

inside the glove box. Thermal behaviors of the electrodes were analyzed on a TGA (TGA7, USA) instrument with temperature ramping from room temperature to 500 °C. Scanning electron microscopy (SEM) was conducted on JSM-6380 (Japan). Transmission electron microscopy (TEM) was performed on JEM-2100HR (Japan). X-ray diffraction (XRD) was carried out on BRUKER D8 ADVANCE (Germany) with monochromatized Cu K α radiation. XPS (ESCALAB 250) was conducted using a focused monochromatized Al K α radiation ($h\nu = 1486.6 \text{ eV}$). The graphite peak at 284.8 eV was used as a reference for the final adjustment of the energy scale in the spectra.

2.4. Computational Methods

The energy levels of the highest occupied molecule orbital (HOMO) of the electrolyte solvents and the additive were calculated by using the Gaussian 09 package. The method used for full geometry optimization was the density functional theory (DFT) with B3LYP in conjunction with the 6–311++G (d, p) basis set. Polarized continuum models (PCM) were used to investigate the bulk solvent effect (dielectric constant is 20.5).

3. Results and discussion

3.1. Self-discharge of charged NCM

Fig. 1 presents the self-discharge profiles of $\text{Li}/\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cells after three charge/discharge cycles at C/5 in standard and TMSP-containing electrolytes. It can be seen from Fig. 1 that, after storage for 20 days, the potential of the cathode charged to 4.5 V in standard electrolyte decreases to 0.5 V. It is apparent that the charged $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ suffers serious self-discharge in standard electrolyte.

When the end-of-charge potential of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ falls outside the electrochemical stability window of the carbonate-based electrolyte, which is about 4.2 V [20], the standard electrolyte tends to lose electrons and oxidatively decomposes on the surface of charged $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. Accordingly, the Co^{3+} and Ni^{4+} on the surface of the charged $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ are reduced to Co^{2+} and Ni^{3+} or Ni^{2+} , corresponding to the potential plateaus at 4.0–4.5 V and 3.7–4.0 V, respectively, which are accompanied with lithium insertion into the layered structure and do not involve any phase transition [29]. These reactions proceed concurrently without any potential limitation, unlike charge/discharge cycling in which the reductions of transition

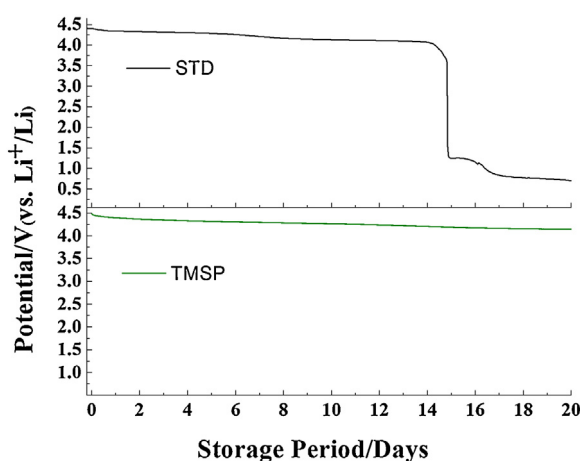


Fig. 1. Self-discharge profiles of $\text{Li}/\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cells after three charge/discharge cycles at C/5 in standard and TMSP-containing electrolytes.

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