



Contents lists available at ScienceDirect

Applied Energy

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

Application of tris(trimethylsilyl)borate to suppress self-discharge of layered nickel cobalt manganese oxide for high energy battery

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HIGHLIGHTS

- TMSB is an effective additive for self-discharge suppression of charged LNCM under 4.5 V.
- SEI film is formed on LNCM at initial stage of cycling due to preferential oxidation of TMSB.
- Electrochemical oxidation decomposition of electrolyte during charge under 4.5 V is suppressed.
- Chemical interaction between charged LNCM and electrolyte during storage is avoided.

ARTICLE INFO

Article history:

Received 5 January 2016
Received in revised form 10 March 2016
Accepted 29 March 2016
Available online xxx

Keywords:

Layered nickel cobalt manganese oxide
High potential
Self-discharge
Solid electrolyte interphase
Electrolyte additive

ABSTRACT

Tris(trimethylsilyl)borate (TMSB) is applied to suppress the self-discharge of charged $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (LNCM) under high potential. The contribution of TMSB is understood via physical and electrochemical characterizations. It is found that the charged LNCM under 4.5 V suffers serious self-discharge: potential drops to 0.5 V and crystal structure collapses, but this self-discharge is effectively suppressed by applying TMSB in a standard (STD) electrolyte. Different from the failure from cycling, which is caused mainly by the electrochemical oxidation decomposition of electrolyte, the self-discharge results from the interaction between charged LNCM and electrolyte. TMSB is preferentially oxidized in comparison with STD electrolyte, generating a solid electrolyte interphase film on LNCM, which avoids the direct contact between LNCM and electrolyte and thus suppresses the self-discharge of the charged LNCM.

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1. Introduction

Li-ion battery (LIB) is a promising power source for electric vehicles [1–3]. To enhance the energy density of LIB, the cathodes with higher specific capacity and operating potential than currently commercialized ones (LiFePO_4 , LiCoO_2 , LiMn_2O_4 , etc.) need to be developed [4–6]. A layered oxide, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (LNCM), has attracted much attention due to its advantages compared with commercialized cathodes, including larger reversible capacity, better environmental benignity, lower cost, and most importantly its additional specific capacity by enhancing the charging potential [7–10].

However, LNCM exhibits poor cyclic stability under high potential [11–15] and the LNCM after charging under high potential suffers serious self-discharge [16–20]. The mechanism involved in cyclic stability deterioration of LNCM has been well understood. The failure of LNCM from cycling is caused mainly by the electrochemical oxidation decomposition of electrolyte under high potential, which generates gaseous products such as carbon dioxide and polymer deposits such as oligomer of alkyl carbonates [21,22]. Additionally, HF is also formed, because the electrolyte decomposition takes place in the form of the complexes between solvent carbonate molecules and salt anion PF_6^- , leading to the dissolution of transition metal ions in cathodes.

Various methods have been applied to improve the cyclic stability of cathodes under high potential [23–28]. Among these methods, the approach based on electrolyte additives is most attractive because a protective solid electrolyte interphase (SEI)

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film can be generated by applying the additives in electrolyte. The SEI film provides a protection for cathodes and suppresses the electrochemical oxidation decomposition of the electrolyte [29]. Tris(trimethylsilyl)borate (TMSB) has been successfully applied to improve the cyclability of various cathodes including $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}]\text{O}_2$ [30], $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [31] and LiMn_2O_4 [32], which is based on the SEI film formed by TMSB. It has been known that TMSB is oxidized electrochemically more easily than the electrolyte and SEI film is formed from its oxidation decomposition products, silicon and boron-containing compounds [30]. Unlike the electrolyte decomposition, no gaseous products are formed from TMSB decomposition and the resulting SEI film can provide a protection for cathodes.

Compared with the intensive interest in the mechanism on and the solution to the cyclic stability deterioration of LNCM, less attention has been given to the self-discharge mechanism of LNCM, not to mention the solution to the self-discharge [18,33–35]. On the base of our previous understandings on the self-discharge mechanism [18] and the effectiveness of TMSB for suppressing the self-discharge of 5 V $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [34], we reported the application of TMSB as an electrolyte additive to suppress the self-discharge of 4.5 V LNCM in this work. Physical and electrochemical characterizations have been performed to understand the contribution of TMSB.

2. Experimental and calculation

2.1. Preparation

Battery-grade solvents of ethylene carbonate (EC) and dimethyl carbonate (DMC) and salt (LiPF_6) were provided by Guangzhou Tinci. TMSB was purchased from Fujian Chuangxin. The electrolytes used were 1.0 M LiPF_6 in mixed solvent of EC and DMC (EC:DMC = 1:2) without (STD) and with TMSB (1 wt.%). This TMSB concentration was selected based on our previous optimization for the cyclic stability improvement of 5 V $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [31]. LNCM electrode was made by coating a mixture of LNCM (Qingdao Xinzheng, 80 wt.%), acetylene carbon black (10 wt.%), and PVdF (10 wt.%) onto an Al current collector. $\text{Li}/\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ coin cells (2025-type) were assembled with Celgard 2400 separators, electrolyte, lithium foil anode, LNCM cathode in a glove-box (Ar atmosphere), where the contents of H_2O and O_2 were controlled to less than 0.1 ppm and 10 ppm, respectively.

2.2. Electrochemical measurements

For self-discharge test, LNCM electrode was charged/discharged at C/5 (1 C = 165 mA g^{-1}) for two cycles between 3.0 and 4.5 V on Land CT2001A (China), and the potential of the charged LNCM electrode was recorded at open circuit potential. Chronoamperometry (CA) was conducted on Solartron-1480 (England).

2.3. Physical characterizations

The cycled LNCM electrodes were rinsed by using DMC and dried in the glove box for physical characterizations. SEM was conducted on JSM-6380 (Japan). TEM was performed on JEM-2100HR (Japan). TGA was performed on TGA7 instrument (USA) from room temperature to 500 °C, at a heating rate of 10 °C min^{-1} in the nitrogen atmosphere. XRD was performed on BRUKER D8 ADVANCE (Germany) with monochromatized Cu K α radiation. XPS was conducted on ESCALAB 250 with Al K α radiation ($h\nu = 1486.6$ eV). The energy scales was adjusted based on the graphite at 284.8 eV.

2.4. Computational methods

The highest occupied molecule orbital energy levels of TMSB and solvents were obtained by calculations based on Gaussian 09 package. The equilibrium states of reactants and products were optimized with B3LYP with the 6-311++G (d) level basis set. The oxidation potential was obtained based on Eq. (1) [36].

$$E_{\text{ox}}(\text{Li}^+/\text{Li}) = [G(\text{M}^+) - G(\text{M})]/F - 1.4 \text{ V} \quad (1)$$

where $G(\text{M})$ and $G(\text{M}^+)$ are the free energies of reactant M and its product M^+ at 298.15 K in solvent, respectively, and F is Faraday constant. Polarized continuum models (PCM) were adopted (dielectric constant is 20.5).

3. Results and discussion

3.1. Potential variation of charged LNCM

The charge/discharge behavior of LNCM was evaluated firstly. Fig. 1 shows the initial and second charge/discharge curves of LNCM in STD (Fig. 1A) and TMSB-containing (Fig. 1B) electrolytes at C/5 between 3.0 and 4.5 V. LNCM behaves similarly in STD and TMSB-containing electrolytes: delivering a discharge capacity of as high as 200 mA h g^{-1} and possessing a slope charge–discharge profile with a low coulombic efficiency at first cycle and an

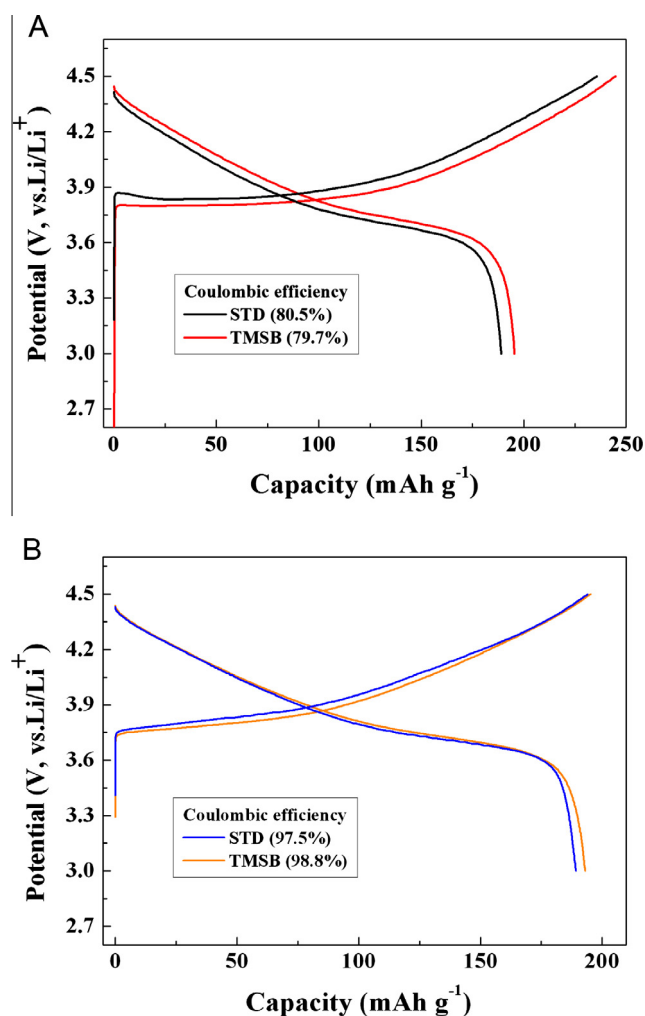


Fig. 1. The initial (A) and second (B) charge–discharge curves of LNCM in STD and TMSB-containing electrolytes at C/5.

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