



Interaction between cathode and anode and its impact on the production of alkyl dicarbonates in lithium ion batteries



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ABSTRACT

A new simple storage experiment is introduced to show direct evidence of a cathode-anode interaction. The delithiated positive electrodes and/or the lithiated negative electrodes from Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O₂/graphite and LiCoO₂/graphite pouch cells are stored in Nalgene bottles (high-density polyethylene) filled with 1.0 M LiPF₆ in an ethylene carbonate: diethyl carbonate (EC:DEC, 1:2 v/v ratio) electrolyte for 2 weeks in an Ar-filled glove box at room temperature. During the storage experiment, the color change of the electrolyte, the formation of alkyl dicarbonates, and the decomposition of LiPF₆ are observed. The most important result of this storage experiment is that these reactions are significantly affected by the cathode-anode interaction. The electrolyte color change comes with slightly larger impedance growth during cycling and the alkyl dicarbonates improve coulombic efficiency. The decomposition of LiPF₆ is suppressed by the negative electrode. The experiment and results shown here will be helpful to those who want to research the cathode-anode interaction and improve the performances of Li-ion batteries.

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1. Introduction

Li-ion batteries operate by Li ions migrating through electrolyte and the intercalation/deintercalation between the positive electrode and the negative electrode. It is not surprising if certain molecular compounds can form from parasitic reactions between components such as electrolytes and electrodes during the operation of Li-ion batteries. The materials produced might migrate through electrolytes between the electrodes during storage or cycling and be able to react at the surface of the electrodes, which could affect the performances of Li ion batteries in several ways.

Recently Li et al. proved that a cathode-anode interaction existed by using “back-to-back” LiNi_{0.5}Mn_{1.5}O₄/Li₄Ti₅O₁₂ (LNMO/LTO) cells. They also investigated the effects of substituting transition metal ions in LNMO, electrolyte salt, and electrolyte additives on the cathode-anode interaction and the performances of LNMO/LTO cells [1–3]. These results suggested that the cathode-anode interaction significantly affected the performances of LNMO/LTO cells.

There have also been a number of studies that suggested the existence of a cathode-anode interaction and investigated the effects of its products on Li-ion cells [4–9]. Wang et al. suggested

that acidic impurities formed at the positive electrode could migrate to the negative electrode and destroyed the SEI layer, which could lead to irreversible capacity loss during high temperature storage [4]. Aurbach et al. suggested that lithiated graphite particles could migrate from the negative electrode to the positive electrode. The lithium ions intercalated in the migrated graphite particles reacted with the positive electrode and caused reversible capacity loss [5]. Sloop et al. proposed that CO₂ formed by the reaction between LiPF₆ and solvents was reduced at the negative electrode to oxalate and re-oxidized to CO₂ at the positive electrode, which caused a reversible self-discharge by a “shuttle” mechanism [6]. Dedryvere et al. suggested that a passivation film on the surface of the Li₄Ti₅O₁₂ negative electrode was created by organic species formed at the positive electrode [8]. Burns et al. suggested that electrolyte oxidation products created at the positive electrode migrated to the negative electrode and formed a solid layer on the front surface of the negative electrode, which significantly affected the cyclelife of Li-ion batteries [9]. As shown in these studies, the cathode-anode interaction seems to play an important role in the performance of Li-ion cells.

In this paper, we will introduce a very simple storage experiment that shows direct evidence of a cathode-anode interaction by using 1.0 M LiPF₆ in an EC:DEC (1:2 v/v ratio) electrolyte and the electrodes recovered from charged Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O₂/graphite (NMC) and LiCoO₂/graphite (LCO) pouch cells. This experiment only included electrolyte and charged electrodes so that any unwanted side reactions caused by the other parts of

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the pouch cells can be ignored. The results of these experiments are divided into 3 topics: the color change of the electrolyte, the production of alkyl dicarbonates, and the decomposition of LiPF_6 , which were investigated by using various measurement methods. Ultraviolet–visible spectroscopy (UV–Vis), gas chromatography coupled with electron impact mass spectroscopy (GC–MS), Maccor series 4000 cyler, electrochemical impedance spectroscopy (EIS), accelerating rate calorimetry (ARC), and nuclear magnetic resonance (NMR) were used for this study. This paper will help those who want to further investigate cathode–anode reactions.

2. Experimental

1.0 M LiPF_6 in EC:DEC (2:1 v/v ratio) was used as an electrolyte. Dry $\text{Li}[\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}]\text{O}_2/\text{graphite}$ (NMC, nominal 220 mAh) pouch cells and dry $\text{LiCoO}_2/\text{graphite}$ (LCO, nominal 310 mAh) pouch cells were fabricated for a 4.2 V operation. The pouch cells were dried overnight at 80 °C under a vacuum to remove any water impurities before the electrolyte filling process. 0.85 g and 1.0 g of electrolytes were injected into the NMC and LCO pouch cells, respectively, in an Ar-filled glove box. The cells were vacuum-sealed with a compact vacuum sealer (MSK-115A, MTI Corp.) after the electrolyte was filled. Then, the cells were moved to a 40. ± 0.1 °C box and held at 1.5 V for 24 hours for complete wetting of the electrolyte. During the formation process, the cells were charged at a rate of C/20 to 4.2 V in the 40. ± 0.1 °C box. After charging, the cells were transferred into the Ar-filled glove box, and cut open to recover the delithiated positive electrode and the lithiated negative electrode.

To investigate the cathode–anode interaction, 7 Nalgene bottles filled with 1.0 M LiPF_6 in an EC:DEC (2:1 v/v ratio) electrolyte were prepared and 6 different combinations of the electrodes were put into the bottles: 1) a delithiated NMC electrode from NMC pouch cells (N+), 2) a lithiated graphite electrode from NMC pouch cells (N–), 3) both delithiated NMC and lithiated graphite electrodes from NMC pouch cells (N+–), 4) a delithiated LCO electrode from LCO pouch cells (L+), 5) a lithiated graphite electrode from LCO pouch cells (L–), and 6) both delithiated LCO and lithiated graphite electrodes from LCO pouch cells (L+–). The last bottle was filled with the only electrolyte (without any electrodes) and used as the control electrolyte solution (control). The bottles 3 (N+–) and 6 (L+–) included the separator recovered from the pouch cells between the positive electrode and the negative electrode to avoid a short circuit. And all the other bottles also included a small piece of separator for comparison. The 7 bottles were stored in the Ar-filled glove box for 2 weeks at room temperature. After storage, the electrolytes were recovered and filtered to remove any floating electrode particles, and then these electrolytes were used for various experiments.

Symmetric and full coin cells were fabricated using the 7 electrolyte solutions, fresh electrodes recovered from NMC pouch cells, and the 2 layers of poly-ethylene separator between the electrodes. And the effect of the 7 electrolyte solutions on the positive electrode and the negative electrode was investigated separately. This was done by measuring cyclife and impedance growth during cycling. The procedure of making symmetric cells is described in detail in references [10–12]. Full coin cells were cycled between 2.8 V and 4.2 V and symmetric cells were cycled between –1.2 V and 1.2 V at a rate of C/5 in a 30. ± 0.1 °C box for 15 cycles on the Maccor series 4000 cyler.

NMC/graphite pouch cells with 2 wt% diethyl-2,5-dioxahexane carboxylate (DEOHC, TCI America) and 2 wt% dimethyl-2,5-dioxahexane carboxylate (DMOHC, TCI America) in 1.0 M LiPF_6 EC:DEC (2:1 v/v ratio) were fabricated and cycled to investigate the effect of DEOHC and DMOHC on cyclife and impedance growth during cycling. The chemical structure of DMOHC and DEOHC are

shown in Fig. 1. Pouch cells were cycled between 2.8 V and 4.2 V at a rate of C/10 in a 40. ± 0.1 °C box for 15 cycles on the Maccor series 4000 cyler.

Electrochemical impedance spectroscopy (EIS) measurements for the pouch cells and coin cells were also performed. The coin cells and pouch cells were charged to 3.8 V and then moved to a 10. ± 0.1 °C box for EIS measurement. The frequency range of impedance data was from 100 kHz to 20 mHz with a signal amplitude of 10 mV.

UV–Vis was used to compare the colour change after the storage experiment. The UV–Vis spectra of the 7 samples were collected using an Agilent Cary 60 spectrophotometer at room temperature in the air. Teflon-capped cuvettes were used to suppress contact with the air (square shape, 10 mm path length, and 1 mm quartz thickness).

GC–MS analysis for the electrolyte solutions was conducted using a Bruker 436-GC. A split/split-less injector and a BR-5MS 30 m column with an inner diameter of 0.25 mm and a coating thickness of 1 μm were used together. The detailed procedure of the GC–MS sample preparation and the experiment condition is shown in reference [13].

The effect of the electrolyte solutions on the thermal stability of NMC positive electrode material was investigated using ARC. The NMC powder used here for the ARC experiment was obtained from dry NMC pouch cells. The detailed procedure of ARC sample preparation and the experiment condition is shown in references [14–16].

^{19}F -NMR spectra of the electrolyte solutions were collected to investigate the decomposition of LiPF_6 by using a Bruker Avance 300 spectrometer (282.42 MHz ^{19}F Larmor frequency). Fluorine chemical shifts were referenced with respect to CCl_3F . Glass NMR tubes were used for the measurements and acetone- d_6 was used as the solvent. The samples were prepared in an Ar-filled glove box and immediately transferred to an NMR spectrometer to avoid any reaction between HF and glass NMR tubes caused by water contamination [17,18].

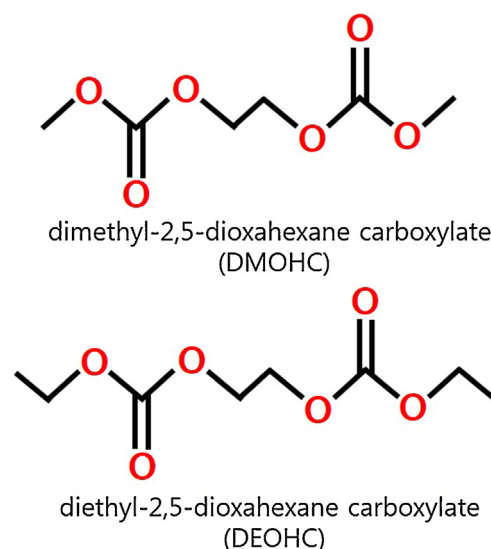


Fig. 1. Chemical structure of dimethyl-2,5-dioxahexane carboxylate (DMOHC) and diethyl-2,5-dioxahexane carboxylate (DEOHC).

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