



Enhanced cycling performance of lithium metal secondary batteries with succinic anhydride as an electrolyte additive



Gi-Beom Han^{a,1}, Je-Nam Lee^{a,1}, Dong Jin Lee^a, Hongkyung Lee^a, Jongchan Song^a, Hyewon Lee^b, Myung-Hyun Ryou^b, Jung-Ki Park^{a,**}, Yong Min Lee^{b,*}

^a Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong-gu, Daejeon, 305-701, Republic of Korea

^b Department of Chemical and Biological Engineering, Hanbat National University, Deokmyung-dong, Yuseong-gu, Daejeon, 305-701, Republic of Korea

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ABSTRACT

The effect of succinic anhydride (SA) as an electrolyte additive on the cycling performance of Li electrode is discussed. As the SA content in the electrolyte increased from 2 to 5 to 10 wt%, the capacity retention of LiCoO₂/Li cell is greatly improved owing to the modification of the solid electrolyte interphase (SEI) layer and the suppression of dendrite growth on the Li electrode. In particular, when 10 wt% SA is introduced into the electrolyte, the Li electrode thickness increases only about 45 μm (from 100 to 145 μm) after 40 cycles, whereas an increase of about 210 μm occurs without SA. This amazing enhancement in cycling performance is also augmented by a much smaller increase in the bulk resistance of the LiCoO₂/Li cell after cycling with 10 wt% SA.

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1. Introduction

Li negative electrode has a theoretical capacity of 3862 mAh g⁻¹ and the lowest observed redox potential of -3.04 V (vs. SHE), so it has been attractive candidates for high-energy-density lithium secondary batteries [1,2]. However, commercialization of lithium secondary batteries has only been achieved with Li-insertion-based carbon electrode. Because of safety problem caused by the dendrite formed on the surface of Li electrode during Li ion deposition, which can result in internal short-circuit of the cell [3,4]. Nevertheless, recent demand for high-energy-density secondary batteries such as Li-O₂ [5–7] and Li-S [5,8,9] batteries has meant that metallic Li electrode is being revisited.

Apart from the abovementioned safety issue, Li electrode is known to suffer from poor cycling performance because of the electrolyte depletion associated with the dendrite growth due to the reactivity of Li electrode, especially at high current rate [10,11]. To solve these problems, various approaches to improve the cycling performance of Li electrode have been reported. For instance, Li electrode surface has been coated by

protective layer to prevent direct contact between Li electrode and the liquid electrolyte [12,13], and Li powder electrode with large surface area was also investigated as a means to reduce the current density of the electrode [14]. These surface treatment or structure control could result in impressive enhancements in the cycling performance of Li electrode. However, considering drastic change of in the morphology of the Li electrode during charge/discharge and the overall cell fabrication process, introduction of electrolyte additive, one of the most effective methods of enhancing battery performance, would still be a prerequisite for achieving improved cycling performance of practical Li electrode [15].

Herein, we introduce succinic anhydride (SA) as a new and effective electrolyte additive for Li electrode. The effect of amount of SA on the cycle performance of the Li electrode was examined and correlated with the observed morphological changes of the Li electrode. For this purpose, scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS) were performed to characterize the effect of SA on Li electrode.

2. Experimental

2.1. Cell preparations and electrochemical measurements

A solution of 1 M lithium hexafluorophosphate (LiPF₆) solution in ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) with 1:1:1 volume ratio was provided by

* Corresponding author. Tel.: +82 42 821 1549; fax: +82 42 821 1692.

** Co-corresponding author. Tel.: +82 42 350 3965; fax: +82 42 350 3910.

E-mail addresses: jungpark@kaist.ac.kr (J.-K. Park), yongmin.lee@hanbat.ac.kr (Y.M. Lee).

¹ Both authors contributed equally to this work.

PANAX ETEC (Korea) and used as the reference electrolyte. The electrolyte additive, SA, was purchased from Aldrich and was used without further purification. The amount of SA introduced in the reference electrolyte was from 2 to 10 wt%.

Pouch-type two-electrode cells were used in the cycling tests. Li metal (Honzo Metal) laminated on Cu foil (20 μm) was used as the anode, and LiCoO_2 electrode on Al foil was used as the cathode. The cells were fabricated by sandwiching a polyethylene (PE) separator (20 μm) between the LiCoO_2 and Li electrodes. Before assembly, the LiCoO_2 electrodes and separators were thoroughly soaked with electrolyte for 24 h to fill the pores in the electrodes and separators. The loading amount of LiCoO_2 is 11.5 mg/cm^2 , and the Li anode capacity is 13.7 times higher than the cathode.

A computer-controlled battery measurement system (TOSCAT 3000, Toyo System) was used in the charge/discharge tests. The assembled cells were aged for 12 h then precycled in the potential range of 3.0 ~ 4.2 V at a constant current of 0.15 mA/cm^2 (C/10 based on LiCoO_2/Li cell) for 1 cycle. Then, they were cycled at a constant current of 0.5 C to 4.2 V and subsequently at a constant voltage of 4.2 V to 0.1 C for charging, and at a constant current of 0.5 C to 3.0 V for discharging. Both the precycling and cycling were performed at room temperature.

EIS measurements were conducted using a Solartron 1400 frequency response analyzer (FRA) in conjunction with a Solartron 1470E electrochemical interface in a frequency range of 10^6 – 10^{-1} Hz.

2.2. Surface morphologies and composition analysis

Surface and cross-sectional FE-SEM (field emission scanning electron microscope, Sirion, FEI) images of the Li electrodes after precycling and cycling were comparatively examined. Li electrodes were dismantled after precycling and after cycling and were washed in dimethyl carbonate (DMC) to remove the residual electrolyte solvent and LiPF_6 salt and then dried in a vacuum chamber for 12 h at room temperature before analysis. Each cross-sectional image was obtained by tilting the Li electrodes. The composition of the SEI layer on the Li electrodes was analyzed by performing using XPS (ESCALAB 250, VG Scientifics). All the high-resolution XPS profiles were calibrated based on the C 1s peak at a binding energy of 285 eV. All the electrolyte preparation, cell assembly, disassembly, and electrode washing processes were executed in an Ar-filled glove box (MOTTEK) with water and oxygen contents of 1 ppm.

3. Results and Discussion

3.1. Capacity fading behavior of LiCoO_2/Li and $\text{LiCoO}_2/\text{graphite}$ cells

Before the effect of SA on the cycling performance of Li electrodes was investigated, we compared the cycleability between $\text{LiCoO}_2/\text{graphite}$ and LiCoO_2/Li cells to confirm their capacity fading behavior (Fig. 1). The $\text{LiCoO}_2/\text{graphite}$ cell does not exhibit rapid capacity decay during cycling, whereas the capacity of the LiCoO_2/Li cell fades rapidly after 30 cycles. Based on the cycling behavior of these two cells, it is certain that the sudden capacity fading of LiCoO_2/Li cell originates from the Li electrode, because the same LiCoO_2 electrode in $\text{LiCoO}_2/\text{graphite}$ cell does not lead to such sudden capacity fading during cell operation.

3.2. Electrochemical characteristics of SA and the cycling performance of LiCoO_2/Li cell

The cathodic and anodic decomposition behavior of SA was investigated using the linear sweep voltammetry (LSV) technique. The detailed experimental procedure is presented elsewhere

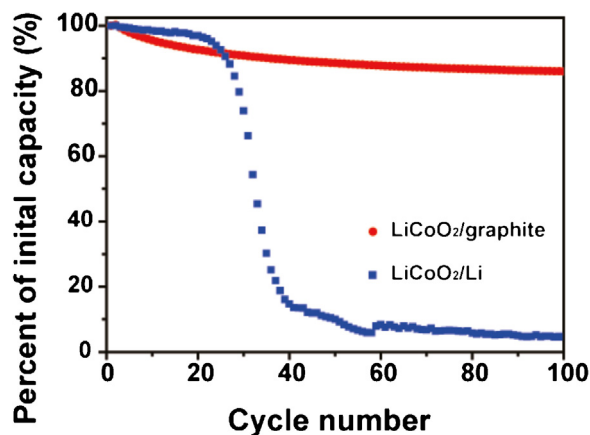


Fig. 1. Comparison of the cycleability between $\text{LiCoO}_2/\text{graphite}$ and LiCoO_2/Li cells.

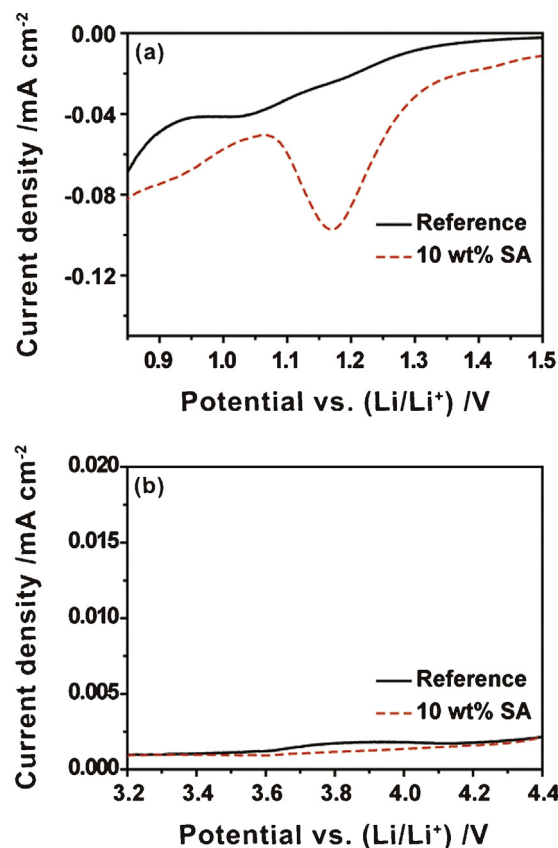


Fig. 2. Linear sweep voltammetry (LSV) profiles of (a) reductive sweep at the rate of 0.1 mV s^{-1} (Graphite/electrolyte/Li) and (b) oxidative sweep at the rate of 0.1 mV s^{-1} (SUS/electrolyte/Li) with and without SA.

[16,17]. Fig. 2a shows the cathodic LSV data for the electrolytes with and without SA. The cathodic current increases upon introduction of 10 wt% SA and shows a peak at about 1.2 V vs. Li/Li^+ . This indicates that SA can be a useful electrolyte additive for the Li electrode, because the operation potential of the Li electrode is far below the reductive decomposition potential of SA. Furthermore, the anodic LSV data in Fig. 2b show that there is no oxidation decomposition of SA during the operation conditions. As a result, it is expected that SA will act only as an electrolyte additive for the Li electrode.

Fig. 3a and b compare the precycling profiles and capacity retentions of LiCoO_2/Li cells with different amounts of SA in the electrolyte. As shown in Fig. 3a, there is no significant change in the

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