

Effects of binder content on manganese dissolution and electrochemical performances of spinel lithium manganese oxide cathodes for lithium ion batteries



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ABSTRACT

In this study, the effects of the polyvinylidene fluoride (PVdF) binder on the Mn dissolution behavior and electrochemical performances of LiMn_2O_4 (LMO) electrodes are investigated. It is found that increasing the PVdF content (3, 5, 7, and 10 wt.%) leads to reduced Mn dissolution, and thus superior cycle performance at elevated temperature (60 °C). This can be ascribed to increased binder coverage on the LMO surface, as evidenced by X-ray photoelectron spectroscopy measurements, which acts a role as a passivation layer for Mn dissolution. The rate capability of the LMO electrode is hardly deteriorated as the PVdF content increases, despite the increasing surface coverage. Electrochemical impedance measurements reveal that the LMO electrode with higher binder loading exhibits lower electrode impedance, which is suggested to be due to enhanced electronic passage through the composite LMO electrode.

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1. Introduction

LiMn_2O_4 (LMO) is a promising cathode material for lithium ion batteries (LIBs), mainly due to its superior electrochemical properties and competitive cost [1–3]. Nevertheless, severe capacity fading related to Mn dissolution, especially at elevated temperature, remains the most critical issue of LMO cathodes [4–14]. The Mn-dissolution reaction proceeds mainly through disproportionation reaction; $\text{Mn}^{3+}(\text{electrode}) \rightarrow \text{Mn}^{4+}(\text{electrode}) + \text{Mn}^{2+}(\text{electrolyte})$ [4–11]. Moreover, the dissolved Mn^{2+} is known to accelerate the degradation of the anode [11–14]. In order to suppress Mn dissolution, extensive studies have been focused on modification of the electrode materials [15–17] or using electrolyte additives [18–23]. Meanwhile, the strategy of optimizing the composition of inactive components (polymeric binder and conductive carbon), particularly to reduce Mn dissolution, has gained little attention.

Polymeric binder is an essential electrode component that provides adhesion among the particles of active materials and

between active materials and current collectors [24–26]. Besides the fundamental role of offering mechanical integrity, recent reports claim that such binders also affect the LIB performances via variations in their electronic and ionic conduction. Highly conductive and adhesive polyfluorene-type binders significantly improved the electrochemical performance of high-capacity silicon electrodes by maintaining the electrical network during the charge/discharge processes [27,28]. Because a portion of the surface of the active materials is covered with the binder film [29,30], it is usually preferred that the binder absorb a sufficient amount of electrolyte for Li^+ ion transport to proceed, unless excess electrolyte uptake severely deteriorates binder adhesion [31,32]. Our recent study revealed that the relatively high electrolyte uptake of polyvinylidene fluoride (PVdF) and polyacrylonitrile (PAN) binders led to superior rate performance of the LMO electrodes due to facile Li^+ ion transport, when compared to polyacrylic acid (PAA) and polyvinyl alcohol (PVA) binders [33]. On the other hand, low-electrolyte-uptake binders such as PAA, PVA, alginate, and styrene-butadiene rubber (SBR) were better for high-capacity-silicon anodes, owing to their superior adhesion [30,32,34,35].

Even though the availability of a range of different polymer binders has allowed some improvement in the electrochemical performances of various active materials [36–41], commercial LIB

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cathodes consistently use PVdF as their binder because of its excellent oxidation resistance, thermal stability, and compatibility with active materials [42–44]. Accordingly, it is still valuable to conduct detailed studies on PVdF in order to improve the electrochemical performances of promising cathode materials that incorporate this binder. Liu et al. [45–47] recently reported that the total amount of PVdF and acetylene black, and the PVdF-to-acetylene black ratio, significantly affect not only physical properties (electronic conductivity and porosity), but also electrochemical performances (specific capacity, rate capability, and impedance) of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes. These results were explained by competition between the ion-blocking effect of PVdF and the electronic conducting effect of acetylene black. Moreover, our recent study has revealed that the Mn-dissolution behavior and electrochemical performances greatly depend on the type of polymeric binder [33]. It is clear that the Mn-dissolution reaction can be suppressed if a large portion of the LMO surface is covered by binder, which serves as a passivation layer retarding Mn dissolution.

Based on the prior findings, we considered that higher polymeric-binder content would be beneficial in further suppressing Mn dissolution. Indeed, the research side employs relatively high content of polymeric binder (5–20 wt.%) for electrode fabrication, while the industry field try to minimize the inactive binder portion (2–4 wt.%) [48]. Therefore, it is critical to understand the impact of binder content on the LIB performances to guarantee the relevance of the research outputs to the practical applications. From this perspective, the effects of PVdF binder content on the Mn-dissolution behavior, high temperature cyclability, and rate capability of LMO electrodes were systematically investigated in this study. The PVdF content was varied in the range of 3–10 wt.% because the mechanical integrity of composite electrode cannot be maintained at lower binder content, and the loss in energy density is too severe at higher content for practical purpose.

2. Experimental

The slurry was prepared employing LMO powder (commercial grade, Posco ESM), Super-P, and PVdF (KF9130, Kureha). The composition of the LMO electrodes was controlled as shown in Table 1. The slurry was mixed using a ball mill (Pulverisette 7, Fritsch) with two 10 mm zirconia beads in a 45 ml zirconia jar. It was programmed to repeatedly rotate in two (clockwise and counter-clockwise) directions eight times at 380 rpm. Each rotation was performed for 8 min so that total mixing time was approximately 1 h. The resulting solution was coated on aluminum foil, and finally dried in a convection oven at 130 °C for 20 min, followed by overnight vacuum drying at 80 °C. The loading and density of the composite electrodes was $8.5 \pm 0.3 \text{ mg cm}^{-2}$ and $2.1 \pm 0.2 \text{ g cm}^{-3}$, respectively.

To examine the Mn-dissolution behavior, one piece of the LMO electrode (14 mm diameter) was stored in a PTFE bottle with 4 ml of the electrolyte at 60 °C for 7 days. The electrolyte was 1 M LiPF_6 in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (3/7 v/v, LG Chem). To account for potential leakage during storage, the closed PTFE bottles were weighed before and after storage, and

Table 1
Composition (wt.%) of LMO electrodes fabricated with various PVdF content.

	3%	5%	7%	10%
LMO	92	90	88	85
PVdF	3	5	7	10
Super-P	5	5	5	5

subsequent analysis was performed only when the weight loss of a bottle was negligible. To determine the dissolved Mn^{2+} concentration, 0.5 ml of electrolyte was sampled and diluted with distilled water by a factor of 10, and then the diluted solution was analyzed using atomic absorption spectroscopy (AA-7000, Shimadzu). To assess binder-coverage of the LMO surface, the elements on the electrode surface were analyzed using X-ray photoelectron spectroscopy (ESCALAB 250, Thermo Fisher Sci.) with an $\text{Al K}\alpha$ X-ray source, scanning from 0 to 1200 eV.

For electrochemical tests, coin cells (2016-type) employing LMO cathodes with various proportions of binder, a Li-metal anode, a polyethylene separator (20 μm , Tonen), and 1 M LiPF_6 EC/EMC (3/7 v/v) as electrolyte were assembled in an Ar-filled glove box. All the cells were cycled initially at 25 °C, over a range of 3.0–4.3 V range, two times with 0.2C constant current (CC) charging followed by 4.3 V constant voltage (CV) charging, and 0.2C CC discharging to complete the formation process. Rate capability testing was carried out for LMO/Li cells with 0.5C CC/CV charging and 0.5C–2C discharging over 3.0–4.3 V at 25 °C. Cycle tests were performed for LMO/graphite cells with 0.5C CC/CV and 0.5C CC over 3.0–4.3 V at 60 °C. Electrochemical impedance measurements were carried out for fully discharged LMO/Li cells after the formation process. All the measurements were performed at room temperature using a potentiostat (Biologic VSP) with a built-in EIS analyzer. The frequency range was 100 kHz to 10 mHz, the ac amplitude was 5 mV, and the dc bias voltage was 3.67 V.

3. Results and discussion

3.1. Effects of binder content on Mn-dissolution of LMO electrodes

To examine the effects of PVdF binder content on the Mn-dissolution behavior, the LMO electrodes fabricated with various proportions of PVdF (3, 5, 7, and 10 wt.%) were stored in an electrolyte solution at 60 °C for 7 days, after which the concentrations of dissolved Mn^{2+} were compared (Fig. 1). It is noted that LMO electrodes with higher binder content show less severe Mn dissolution. The amount of Mn dissolution ranges from 0.05 to 0.1 atomic %, which is similar to the values reported in previous studies [8,9]. It is generally agreed that polymeric binders cover some portion of the electrode surface, whereas the rest of the surface is directly exposed to the electrolyte. Since the ionic conductivity of the polymeric binder film is much lower (ca. $10^{-8} \text{ S cm}^{-1}$ [32,49]) than that of liquid electrolytes (ca. 10^{-2} – $10^{-3} \text{ S cm}^{-1}$ [50–53]), the binder film may serve as a passivation layer retarding the

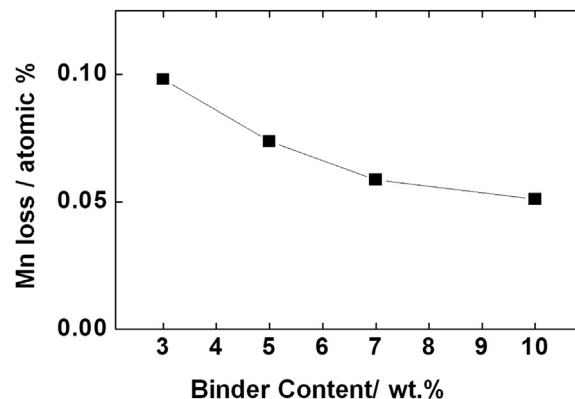


Fig. 1. Concentration of Mn^{2+} dissolved from LMO electrodes fabricated with various proportions of PVdF (3, 5, 7, and 10 wt.%). LMO electrodes were stored in 1 M LiPF_6 EC/EMC (3/7 v/v) at 60 °C for 7 days.

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