



Effects of polymeric binders on electrochemical performances of spinel lithium manganese oxide cathodes in lithium ion batteries



Sangmin Lee ^{a,1}, Eun-Young Kim ^{b,1}, Hochun Lee ^{b,**}, Eun-Suok Oh ^{a,*}

^a School of Chemical Engineering, University of Ulsan, 93 Daehak-ro, Ulsan 680-749, Republic of Korea

^b Department of Energy Systems Engineering, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu 711-873, Republic of Korea

HIGHLIGHTS

- Four types of polymers are adopted as binders for spinel LMO electrodes.
- Binder film on the surface of LMO plays a role of passivation layer for Mn dissolution.
- PAN-LMO electrodes exhibit superior rate capability, thermal stability, and low Mn dissolution.
- PAN is revealed to be an outstanding binder for LMO, compared to PVdF and other binders.

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ABSTRACT

Effects of polymeric binders on both the dissolution of manganese (Mn) and electrochemical properties of spinel LiMn_2O_4 (LMO) electrodes are investigated in detail. Three promising polymers, polyvinyl alcohol (PVA), polyacrylic acid (PAA), and polyacrylonitrile (PAN) are chosen as binders for the LMO electrodes and compared to currently popular polyvinylidene fluoride (PVdF). For LMO electrodes fabricated with the selected binders, physicochemical properties including surface coverage, adhesion strength, and electrolyte uptake are examined. Also, electrochemical performance factors such as Mn dissolution behavior, rate capability, cycle performance, and thermal stability are investigated. PAN is revealed to be an outstanding binder for LMO electrodes based on its excellent rate capability, superior cycle performance, and high thermal stability when compared to the other three binders. This can be ascribed to an appropriate amount of electrolyte uptake and low impedance of the PAN despite the relatively large surface coverage of the LMO that leads to lower Mn dissolution.

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1. Introduction

Due to its superior electrochemical performance, low cost, and environmental inertness, spinel LiMn_2O_4 (LMO) is considered a promising cathode material for lithium ion batteries (LIBs), especially for large scale applications such as electric vehicles and energy storage systems [1,2]. The poor thermal stability of LMO, however, mainly due to manganese (Mn) dissolution at elevated temperatures, has hampered its progress in new applications [3–12]. It is generally known that Mn dissolution is associated with a disproportionation reaction which liberates soluble Mn^{2+} into electrolyte:

$\text{Mn}^{3+}(\text{electrode}) \rightarrow \text{Mn}^{4+}(\text{electrode}) + \text{Mn}^{2+}(\text{electrolyte})$ [2–9]. Then, the dissolved Mn^{2+} moves to the anode and exacerbates degradation of the anode/electrolyte interface, which is revealed to be a key failure mechanism of LMO-based LIBs at elevated temperature [9–12].

So far, extensive studies have been devoted to suppress Mn dissolution, and thus to improve long-term stability of LMO. Most of the attempts have been made to modify the LMO itself in order to enhance its structural stability, [13–15] or to develop functional electrolyte additives to stifle Mn dissolution from LMO or subsequent Mn deposition on the anode [16–21]. In contrast, minimal attention has been paid to the inactive components of LIB electrodes: polymeric binders and conductive carbons [22–25].

In particular, the crucial role of polymeric binders in LIB performance has been recently highlighted [26–31]. The polymeric binder provides integrity within the LIB composite electrode by promoting adhesion among the particles of active materials and between active materials and the current collector. Currently, only

* Corresponding author. Tel.: +82 52 259 2783; fax: +82 52 259 1689.

** Corresponding author. Tel.: +82 53 785 6411; fax: +82 53 785 6409.

E-mail addresses: dukelee@dgist.ac.kr (H. Lee), esoh1@ulsan.ac.kr (E.-S. Oh).

¹ Equally contributed to this work.

two types of binder systems are being widely adopted in the LIB industry: polyvinylidene fluoride (PVdF) dissolved in N-methyl-2-pyrrolidone (NMP) and carboxymethyl cellulose (CMC) combined with styrene-butadiene rubber (SBR) emulsified in water [32–36]. Besides these polymers, a variety of polymers have been recently investigated as potential binders for LIB electrodes such as polyvinyl alcohol (PVA), polyacrylic acid (PAA), polyacrylonitrile (PAN), polyimide (PI), and polysaccharide [28–31,37,38]. Such binders gained attention not only due to their novel binding modes, but also due to their additional properties such as artificial surface passivation for irreversible reactions and mechanical buffer effect for volume change accompanying LIB operation.

PVA binder containing numerous hydroxyl groups in its polymer chain makes strong hydrogen bonds with active materials and the current collector, which is favorable for decreasing volumetric change and preventing excessive electrolyte uptake [30]. PAA binder, the most frequently studied polymer in recent years [28,37,39–42], has been reported to serve as an artificial SEI layer on the surface of active materials. In addition, PAA binder was claimed to be able to maintain the electric network of the SiO anode during cycles, resulting in improved cyclic performance [29]. PAN binder containing a strongly polar nitrile group was also demonstrated to be an efficient binder for various LIB anodes such as graphite, silicon/graphite and lithium titanium oxide [31].

Such studies on binders have mainly focused on LIB anodes. Much less attention has been paid to the cathode side. Although some recent reports claimed that cellulose-based polymers and ionomer binders improved cyclic performance and rate capability of LMO cathodes due to their better structural stability, stronger binding ability and smaller resistance [22,23,43,44], systematic comparison between various binders regarding electrochemical properties of LMO electrodes is still absent. In this study, three promising polymers, PVA, PAA, and PAN as binders for LMO electrodes are compared with the currently most popular PVdF binder. For LMO electrodes fabricated with the selected binders, fundamental properties including surface coverage, adhesion strength, and electrolyte uptake were examined. Then, the Mn dissolution behavior and electrochemical performances of the LMO electrodes were investigated.

2. Experimental

Three commercially available polymers were used as binders: PVdF (KF9130, Kureha), PAN (Mw = 150,000, Aldrich), and PAA (Mw = 3,000,000, Aldrich). Meanwhile high molecular weight PVA with 94% degree of saponification (the number of hydroxyl groups in 100 vinyl units of PVA), which showed excellent binding properties, was synthesized using the procedure described in our previous study [30]. Their chemical structures are shown in Fig. 1.

Cathode slurry was prepared by combining 92 wt.% LMO (commercial grade, Posco ESM) with 3 wt.% Super-p as a conductive material and 5 wt.% binder in n-methyl-2-pyrrolidone solvent. Dimethyl sulfoxide was used as a solvent for PVA binder. The slurry was mixed by 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 both directions 8 times with the rotational speed of 380 rpm. Each rotation was performed for 8 min so that

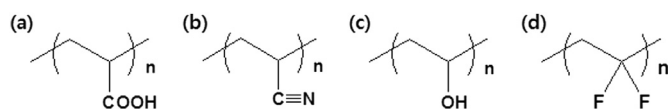


Fig. 1. Chemical structures of the polymers used as binders: (a) PAA, (b) PAN, (c) PVA, and (d) PVdF.

total mixing time was approximately 1 h. The resultant was coated on aluminum foil, and finally dried in a convection oven at 130 °C for 20 min followed by vacuum drying at 80 °C overnight. The loading of the composite electrodes was $10.8 \text{ mg} \pm 0.3 \text{ mg cm}^{-2}$.

The graphite electrode was fabricated by coating a mixture of natural graphite (DAG-87, Sodiff), 1.5 wt.% SBR and 1 wt.% CMC binder on copper foil (10 μm). As an electrolyte, 1 M LiPF_6 in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (3/7 v/v, LG Chem) was used throughout this study.

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. To avoid possible errors due to leakage during storage, the weights of the closed PTFE bottles before and after the storage were checked, and the subsequent analysis was performed only when the weight loss 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 by atomic absorption spectroscopy (AA-7000, Shimadzu). Simultaneously, water and HF contents were analyzed by Karl Fisher (831 KF coulometer, Metrohm) and acid-base titration methods (848 Titrino plus, Metrohm), respectively.

For electrochemical tests, 2016 or 2032-type coin cells employing the LMO cathode containing each binder and a Li-metal or graphite anode with a polyethylene separator (20 μm , Tonen) were assembled in an Ar-filled glove box. All the cells were cycled initially at 25 °C over a 3.0–4.3 V range three times with 0.2C ($1\text{C} = 93.4 \text{ mAh g}^{-1}$) 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 0.2C CC/CV charging and various CC 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, both at 25 °C and 60 °C. Electrochemical impedance spectra (EIS) were obtained for fully discharged LMO/Li cells before and after 24 h storage at 60 °C. 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 3.8 V.

The adhesion strength and surface elements of the LMO electrodes were determined at 180 peel strength measured using a texture analyzer (TA-PLUS, Lloyd), and by X-ray photoelectron spectroscopy (ESCALAB 250, Thermo Fisher Sci.) using an Al K α X-ray source scanning from 0 to 1200 eV, respectively. The electrolyte uptake of the binder films was measured in order to compare the electrolyte wettability of the binder. The pristine binder films (approximately 20 μm) were soaked in electrolyte for 48 h and the change in weight before and after soaking was measured as the amount of electrolyte uptake.

3. Results and discussions

3.1. Effects of binders on Mn dissolution of LMO electrodes

First of all, the effect of polymeric binder on Mn dissolution was investigated by measuring the amount of Mn dissolved from the LMO electrodes prepared with the four types of binders (hereafter called PAA-, PAN-, PVA-, PVdF-LMO, respectively). The electrodes were stored in an electrolyte solution at 60 °C for 7 days and the dissolved amounts of Mn^{2+} including H_2O and HF in the electrolyte were measured and listed in Table 1.

It is noted that PAN- and PVA-LMO exhibit relatively lower amounts of Mn dissolution than PAA- and PVdF-LMO. The amount of Mn dissolution is in the following order: PVA < PAN < PAA \leq PVdF. While the variation in the water content is negligible, the HF

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