



Elevated temperature cycling stability and electrochemical impedance of LiMn_2O_4 cathodes with nanoporous ZrO_2 and TiO_2 coatings

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ABSTRACT

In this study, nanoporous zirconia (ZrO_2) and titania (TiO_2) coatings are shown to stabilize the cycling performance of lithium-ion batteries with LiMn_2O_4 spinel cathodes. The effect of firing temperature on the coating pore size is discussed and the resulting performance of the coated cathodes is evaluated. Stabilization mechanisms, such as neutralization of acidic electrolytes by ZrO_2 and TiO_2 coatings, are examined. It is proposed that the establishment of a complex nanoporous network for lithium-ion transport results in a more uniform current distribution at the particle surface, thereby suppressing capacity fade that may be associated with surface instabilities of the spinel electrode.

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1. Introduction

The rechargeable lithium-ion battery industry has grown tremendously in recent years with the rapid development of portable electronic devices. Lithium-ion battery chemistries are now also being prominently targeted to provide the high gravimetric and volumetric energy densities required by heavy duty applications, e.g., hybrid- and all-electric-vehicles [1–3]. Currently, LiCoO_2 is the dominant cathode material for these batteries. However, for mass electric-vehicle markets, global cobalt supplies may be limited; furthermore, the cost of cobalt is likely to increase significantly as demand continues to grow [4,5]. By comparison, manganese is a plentiful, inexpensive and environmentally friendly element from which the lithium-manganese-oxide spinel, LiMn_2O_4 , can be produced as an alternative cathode material [6,7]. Many studies of LiMn_2O_4 , including cation- and anion-substituted derivatives, have been undertaken that have emphasized its superior safety and performance advantages over LiCoO_2 [8–18].

Despite advantages in terms of both cost and safety, lithium-ion cells with LiMn_2O_4 spinel cathodes have limitations. Chief among these is a decrease in capacity that occurs upon repeated cycling

[19–21]. This problem is observable at room temperature, but is exacerbated at higher temperatures. Numerous factors have been shown to contribute to the capacity fade, such as the choice and purity of the electrolyte and the operating voltage window of the cells.

Early experiments with $\text{Li}_x\text{Mn}_2\text{O}_4$ spinel electrodes ($0 \leq x \leq 2$) showed that excessive discharge below 3.0 V resulted in the formation of $\text{Li}_2\text{Mn}_2\text{O}_4$, in which a large crystallographic (Jahn–Teller) distortion (16% change in the c/a ratio) was responsible for the capacity loss [8,22]. Non-equilibrium localized formation of $\text{Li}_2\text{Mn}_2\text{O}_4$ at the particle surface has also been observed, particularly under high rate conditions above 3 V, which can result in subsequent disproportionation reactions to yield Mn(II) and Mn(IV) products, such as MnO and Li_2MnO_3 , or MnO, Li_2O and $\lambda\text{-MnO}_2$ [23–25]. Soluble Mn^{2+} ions can then be transported across the electrolyte to the carbon (graphitic) anode, where they are deposited, adversely affecting cell performance. Mn dissolution can be at least partially mitigated by cation substitution to increase the average Mn oxidation state above 3.5+ (e.g., $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$) and moderating lattice parameter differences (Δa) between the charged and discharged states [23,26–28].

Electrolyte decomposition in lithium-ion cells can form Lewis acids that accelerate the decomposition of LiMn_2O_4 , to form soluble Mn(II) species that leach into the electrolyte [29,30]. Trace amounts of water in the electrolyte can also react with fluoride-based electrolytes, generating hydrofluoric acid (HF), which has been

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implicated as an additional cause of Mn(II) dissolution [31–33]. Rotating disc electrode experiments have shown that Mn(II) dissolution occurs under both discharged (<3.1 V) and charged (>4.1 V) conditions, and is somewhat more pronounced at the higher potentials [34]. Similarly, manganese deposition on graphite anode surfaces has been documented for lithium-ion cells with LiMn₂O₄ spinel cathodes that were charged to 4.3 V [27].

The capacity fade of LiMn₂O₄ spinels has also been partially attributed to the formation of an electronically insulating solid electrolyte interface (SEI) layer that forms on the cathode surface. This process also occurs when cobalt-based cathodes are used [35], but appears to be more complex for the manganese system due to the accompanying formation of undesirable Mn products that further compromise electronic conductivity, resulting in larger polarization losses [36,37]. It has been shown that the conductivity of the SEI layer depends on the type of electrolyte employed, and that SEI formation occurs concomitantly with changes in the bulk resistance of the electrolyte [38]. Surface enhanced Raman spectroscopy has demonstrated that the SEI layer formed by the interaction of LiMn₂O₄ with an electrolyte of 1 M LiPF₆ in EC:DMC (1:1 by vol) was comprised of a complex mixture of λ-MnO₂ along with various alkoxide, carboxylic and carbonate functional groups formed by oxidation of the electrolyte [39]. It has been estimated that the capacity loss associated with the formation of the electronically insulating SEI layer is roughly double the loss that can be attributed to decomposition of the LiMn₂O₄ spinel electrode [40].

In recent years, various types of coatings and thin film deposition procedures have been explored to improve the electrochemical stability of LiMn₂O₄ cathodes in lithium cells [41–52]. For example (1) improved cycling stability was achieved by coating LiMn₂O₄ with MgO and Al₂O₃ precipitated from nitrate salt solutions [42]; (2) LiMn₂O₄ electrodes demonstrated improved stability at 55 °C when coated with ZnO to neutralize harmful acidic species in the electrolyte [43,44] and (3) we reported a stabilizing effect when amorphous ZrO₂, Al₂O₃ and SiO₂ coatings were deposited onto LiMn₂O₄ electrodes from colloidal suspensions using sol–gel techniques [45,46].

Despite the numerous studies in this area, a functional understanding of coated electrodes remains incomplete. It appears likely that at least some of the metal oxide coatings are capable of neutralizing acid species that might arise in the electrolyte. It has also been suggested that the coatings may act as a physical barrier to Mn(II) dissolution by forming epitaxial layers on the underlying coated spinel, or by modifying structure of the spinel surface. The coatings almost certainly have an effect on the SEI layer, which could modify the electronic- and Li⁺-ion conductivity at the particle surface. At this time, it is not yet clear which of these various processes is most important to the stabilization of a LiMn₂O₄ electrode surface; key variables that influence coating efficacy remain to be identified and optimized for most of the coating materials that have been employed to date.

Limited information has been gathered thus far about the surface structures of coated LiMn₂O₄ electrodes or their stabilizing functions. Few of the studies published on this topic have reported on the morphology, heterogeneity, or pore size of the thin films, although it is well known that all of these properties can be influenced by the synthesis, deposition and sintering processes used in sol–gel chemistry [53,54]. For example, our previous studies have shown that the stabilizing effect of a ZrO₂ coating is highly dependent on particle size [46], which is likely to be one of the key parameters that determines the structure of the thin film coating, and is worthy of further characterization.

In this paper, we compare the electrochemical performance of ZrO₂- and TiO₂-coated cathodes, prepared from colloidal suspensions using sol–gel techniques, under a range of different conditions. The data are compared with physically-mixed LiMn₂O₄

and ZrO₂/TiO₂ composite electrodes to discern the relative contributions of acid/base neutralization and surface/interfacial effects to the stabilization of the cathode imparted by the coatings. It is highly likely that our results are relevant, not only to LiMn₂O₄ spinel electrodes, but also to the recently reported family of layered lithium-mixed-metal-oxides that provide exceptionally high capacities (250 mAh g⁻¹) when charged to high potentials (4.6 V) and could similarly benefit from surface stabilization [55,56].

2. Experimental

The stoichiometric lithium-manganese-oxide spinel, LiMn₂O₄ (Carus Corporation), which is more susceptible to surface degradation than stabilized, cation-substituted spinels such as Li_{1+x}Mn_{2-x}O₄ was selected for our studies to quantify the effects of ZrO₂ and TiO₂ coatings [57]. Colloidal ZrO₂- and TiO₂-suspensions were prepared via acid-catalyzed, sol–gel hydrolysis and condensation reactions of zirconium n-propoxide (Gelest) and titanium isopropoxide (Aldrich) using previously reported techniques [54]. The size of primary colloidal solid particles was determined using a ZetaSizer 3000 dynamic light scattering instrument (Malvern Inc.). Cathode materials were prepared by suspending a measured quantity of spinel in a sufficient volume of colloidal suspension to provide a 4% (by mass) coating. Details of the coating technique are described elsewhere [45,46]. The coated materials were fired for 3 h at either 300 or 400 °C with a 2 °C min⁻¹ ramp rate.

To ascertain coating morphologies and the extent of surface coverage, cathode materials were inspected with a Schottky Field Emission Scanning Electron Microscope (LEO Gemini 1530). An in-lens secondary electron detector, with an accelerating voltage of 3 kV, was used to obtain high resolution surface images. To further characterize the porous coatings, sorption isotherms were measured using a Micromeritics ASAP 2010 micropore analysis instrument. Specific surface areas were estimated from Brunauer–Emmet–Teller (BET) analyses of the adsorption data at low relative pressures [58].

Cathode laminates were prepared using 84% LiMn₂O₄ powder mixed with 4% SFG-6 graphite (Timcal) and 4% acetylene black (Cabot) as current collecting media, and 8% polyvinylidene difluoride as binder (Kynar). The materials were mixed into a slurry using 1-methyl-2-pyrrolidinone as the suspending solvent (Aldrich). The slurry was cast onto an aluminum foil current collector using a 200 μm doctor blade. The resulting laminates were dried in air for 4 h at 75 °C at ambient pressure, followed by another 12 h under vacuum to remove any remaining solvent and adsorbed water. Two laminates were also prepared by mixing 4% (by mass) of two types of ZrO₂ powders with the LiMn₂O₄ spinel using a mortar and pestle in order to investigate the extent to which independent ZrO₂ particles in the electrode might neutralize acidic species in the electrolyte. The first laminate contained a commercial submicron ZrO₂ powder (Aldrich), whereas the second laminate contained a sol–gel derived ZrO₂ xerogel prepared from the same zirconium n-propoxide precursor described above. The xerogel was fired for 3 h at 400 °C, and ground separately with a mortar and pestle before it was mixed with the LiMn₂O₄ powder.

Laminates were pinch rolled to consolidate the dry, solid electrode powders; circular (1.6 cm²) cathode discs were punched from these laminates. The punched cathodes were weighed to determine the amount of active spinel (typically 12–16 mg) before being loaded into sealed, stainless steel coin cells (Hohsen CR2032). A lithium foil anode (Aldrich), a tri-layered polyethylene/polypropylene separator (Celgard 2325), and an electrolyte of 1 M LiPF₆ dissolved in 1:1 ethylene carbonate/diethyl carbonate solvent (Merck LP-40) were used as the other cell components. Cells were assembled in a controlled atmosphere argon-filled glove

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