

Mg, Cu-doped Manganese Oxides for Lithium Battery Applications

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Abstract

Magnesium and copper doped manganese oxides, meant for use as lithium battery cathode materials, have been prepared by oxidation of Mn(II) precursors in the presence of Mg(II) and Cu(II) in an aqueous solution at ambient temperature. This oxidation procedure offers numerous advantages such as environmental suitability, cost-efficiency, and good control over the chemical composition and morphology of the synthesized powders. X-ray diffraction of synthesized powders reveals an amorphous structure. Notably, upon charge discharge cycling the material shows little or no capacity fading after gradual fading in the first few cycles. This suggests that the amorphous structure containing magnesium and copper yields a stable material. Electrochemical characterization of these cathode materials showed a specific capacity of 150- 200 mAh/g.

Introduction

A typical lithium battery consists of a lithium anode, a transition metal oxide cathode, and an organic electrolyte containing lithium ions. As the reaction between lithium metal in the anode and the materials in the cathode occurs, electrons are forced to temporarily part from the lithium atoms, so the Li^+ ions can pass through the electrolyte. The electrons meanwhile travel across a conducting wire, which effectively delivers the electric power to the given device. The electrons then reunite with the lithium ions at the cathode site to generally be intercalated by the material. The power delivered by the reaction depends on the potential difference between the lithium metal and the lithium in the cathode material at the time the reaction takes place. For over 20 years, transition metal oxides have undergone relentless research for cathode materials in order to improve the performance of lithium battery systems and to reduce their cost and hazard to the environment.

Manganese oxides have been investigated as cathode materials because of their low cost and non-toxicity. Many crystalline, amorphous, and aerogel forms of manganese oxides have been studied. Crystalline structures of manganese oxides, particularly spinel and layered structures, which have been investigated for battery applications, have so far

either exhibited low intercalation capacity or poor cycling performance. It has been discovered that the electrochemical performance of these crystalline materials suffers significantly from structural instability and low rate kinetics. However, recent results indicate that manganese oxides can be effective as lithium battery cathodes. Electrochemical data obtained for amorphous manganese oxides, particularly, have shown promise with the high lithium intercalation capacities that have been attained.

Amorphous manganese oxides, MnO_x , have seen increasing attention in recent years for lithium battery applications. They have shown dramatically higher specific capacities than crystalline forms of MnO_x . Synthesis of amorphous manganese oxides has been the focus of a few reports where capacities in the range of 160-250 mAh/g have been attained [1-3]. Remarkably, capacities greater than 400 mAh/g were reported by Xu et al for an amorphous manganese dioxide [1]. Cycling performance, however, remains an issue for these high capacity amorphous compounds. Even though the structure of these amorphous compounds does not appear to undergo global phase transformations during repeated intercalation / de- intercalation, it is speculated that the local structure may undergo gradual changes upon cycling [4]. Such local structure changes would inhibit good capacity retention upon insertion and extraction of lithium.

Elemental doping has been considered to improve cycling performance, possibly by stabilizing electrochemically-favorable forms of manganese oxide. When done by hydrothermal synthesis and sol-gel techniques, multivalent-metal doping of crystalline manganese oxides has shown either improved cyclability or improved electronic conductivity [5-7]. There has also been multivalent-metal doping of some amorphous MnO_x compounds with considerable success [8,9]. Additionally, incorporation of metals having only one common oxidized form - lithium (I), sodium (I), potassium(I) and magnesium(II) has revealed improvements of capacity retention [4, 10-12]. Magnesium, particularly, has shown some notable success amongst these elements, though reduction of the lithium intercalation capacity is reported to occur [11, 12].

We discuss a novel solution-based oxidation route to the synthesis of amorphous manganese oxides containing varying concentrations of magnesium and copper. The synthesis route yields materials with nearly perfect capacity retention upon cycling after 9 cycles through 15 cycles. Such performance is better than has been observed with both pure amorphous manganese oxides and copper-doped manganese oxides. Additionally, the synthesis performed allows increased control over parameters that affect the oxidation state of manganese and the morphology of the powder. We also discuss the effects of Mg, Cu-doping on the electrochemical properties of amorphous manganese oxides and copper-doped amorphous manganese oxides as lithium intercalation hosts.

Experimental

A novel synthesis method was attempted in order to prepare Mg, Cu-doped manganese oxides. In particular, redox reactions in aqueous solutions were performed to yield powder precipitates [13].

At room temperature, aqueous solutions of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$, NaOH, and NaOCl were prepared separately and added to 1500 mL of de-ionized water to precipitate a brown fine powder at pH ~ 12.0 . The concentrations of the reagents used in the synthesis are shown in Table 1. The solution was stirred for 1.5 h. The precipitate was separated from the solution by centrifugation, washed with de-ionized water, and freeze-dried. To test for the presence of any un-reacted manganese, copper, or magnesium, additions of NaOH and NaOCl were made to the supernatant. X-ray powder diffraction (XRD) measurements were collected with a Siemens Diffractometer® using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) for structure analysis.

For electrochemical studies, the active material was mixed with 30% carbon black and 10% PTFE powder by weight. Stress was exerted upon the mix to form a film; a hole-punch was then used to shape quarter-inch pellets. Sample pellets were fit between sheets of copper mesh that act as current collectors for the specimens. Samples were then moved to an argon-filled glove box after heating at 80 °C for 24 h under vacuum. A four-electrode cell was used with pure lithium metal as reference and counter electrodes, and 1 M LiClO₄ in propylene carbonate/ethylene carbonate with 1:1 ratio as the electrolyte. Cycling tests were performed at a charge / discharge rate of C/5 (1.0 mole of Li reacted with 1.0 mole of Mn per 5 h) on a Maccor potentiostat.

Results and Discussion

Treatment of the supernatant and electrochemical testing (discussed below) indicated successful incorporation of magnesium and copper into the manganese oxide. The synthesis allowed good control of dopant content in the synthesized material and is inexpensive, which is attractive for large-scale applications. However, the ambient-temperature aqueous solution route raises the possibility that Mg-OH linkages, rather than intended Mg-O linkages, may reside in the structure. The chemical environment of the O bonded to Mg was indeterminable by XRD, as were any effects it could have on the electrochemical performance.

Sample	Cu / Mn	Mg / Mn	NaOH / Mn	NaOCl / Mn
$\text{Mg}_{0.2}\text{Cu}_{0.2}\text{MnO}_x$	0.2	0.2	1.0	4.0

Table 1. Initial concentrations (M) of constituents used in synthesis by molar ratio.

Figure 1 shows X-ray diffraction patterns for copper-doped manganese oxide and for a Mg, Cu-doped manganese oxide with an Mg / Mn concentration ratio of 0.2. Both samples exhibit a similar amorphous structure resembling pure amorphous manganese oxide [4]. For the copper-doped sample, the weak peaks at 37° and 66° correspond to the $\text{Mn}^{4+}\text{-O}$ spacing in an octahedral arrangement [14]. In contrast, the X-ray diffraction pattern for the Mg, Cu-doped sample indicates the presence of magnesium with a broad peak at 45° , as well as a new peak at 18° and increased peaks at 37° and 66° . A difference in sensitivity between the diffractometers used to characterize the copper-doped sample and the Mg, Cu-doped sample may contribute to the peak increase. However, the patterns appear dissimilar enough to suggest that the magnesium concentration has significantly altered the copper-doped manganese oxide structure. This suggestion is further signified by the electrochemical data.

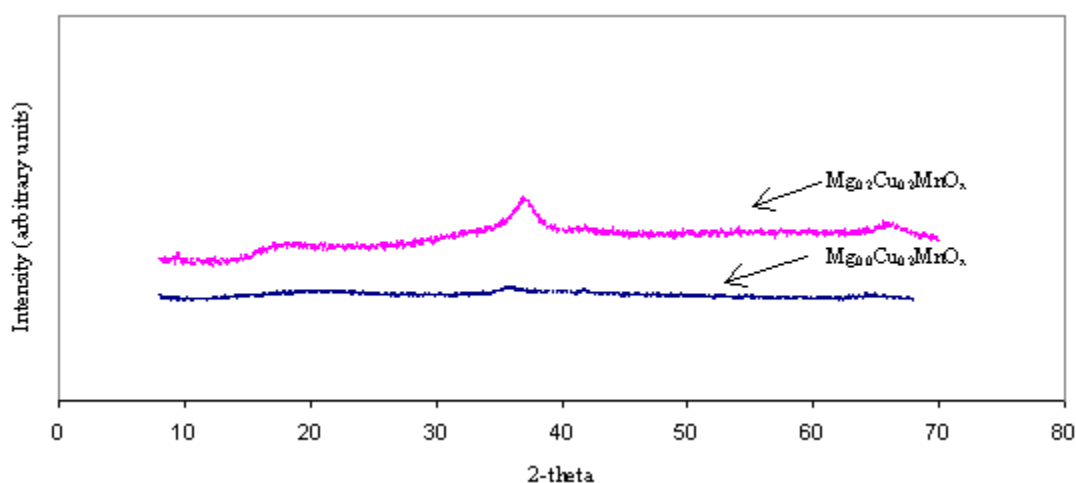


Figure 1. X-ray Diffraction data.

Electrochemical data for Mg-doped and un-doped copper manganese oxide samples is shown in Figure 2. Through 19 cycles, $\text{Mg}_{0.2}\text{Cu}_{0.2}\text{MnO}_x$ shows 100% capacity retention after 10 cycles at ~ 190 mAh/g. This is improved compared to that of the copper-doped amorphous manganese oxide, which exhibits a 0.8% capacity fade per cycle for cycles 10 - 19. For $\text{Mg}_{0.2}\text{Cu}_{0.2}\text{MnO}_x$, it was speculated that the cycling prior to the 10th cycle may have caused a residual concentration of lithium to remain intercalated, which helped to stabilize the structure. An additional electrochemical test with rest steps inserted between cycles was designed in order to possibly promote residual lithium subsidization and further capacity retention (Fig. 3). However, the rest steps did not improve the capacity performance.

Several factors contribute towards capacity fading in manganese oxide cathodes, namely dissolution of Mn^{2+} and problems with structural integrity of the composite cathode. It is plausible that for the doped manganese oxides reported here the amorphous structure is very stable, as shown by the stability in capacity from the 10th -19th cycle; the observed capacity fading may be related to the instability of some local domains

within the globally amorphous structure. Detailed investigations of capacity fading mechanisms of amorphous manganese oxides are necessary and will explain better the nature of stabilization achieved by magnesium and copper doping.

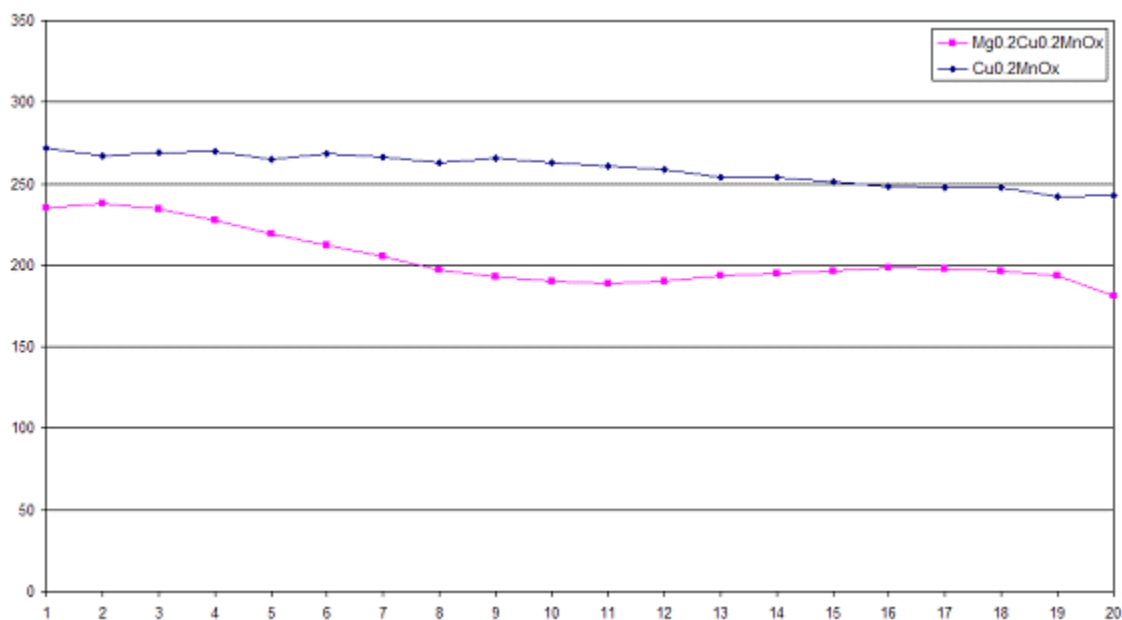


Figure 2. Capacity performance for un-doped and doped copper manganese oxides for cycles 1 - 20 at C/5.

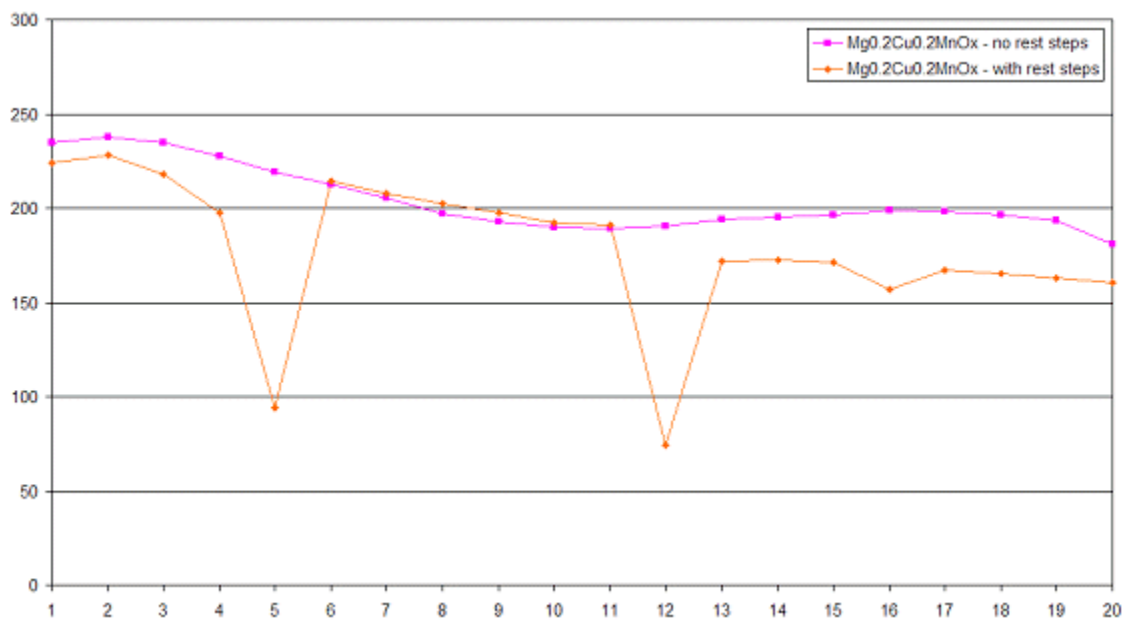


Figure 3. Capacity performance of Mg_{0.2}Cu_{0.2}MnO_x with and without rest steps between cycles.

The reduction in the specific capacity of copper-doped amorphous manganese oxide by the magnesium doping is consistent with the effects of magnesium doping reported by Gummow et al. and Jeong et al. [11,12]. Though the magnesium-doped, spinel-phase manganese oxides reported by Gummow et al. and Jeong et al. maintain improved capacity retention over our synthesized powders, intercalation capacities that they obtained are significantly lower than those of our amorphous materials [11,12]. However, these findings are indicative that divalent doping, particularly with magnesium, is a good way to address the instability associated with manganese oxides as Li-cell electrodes.

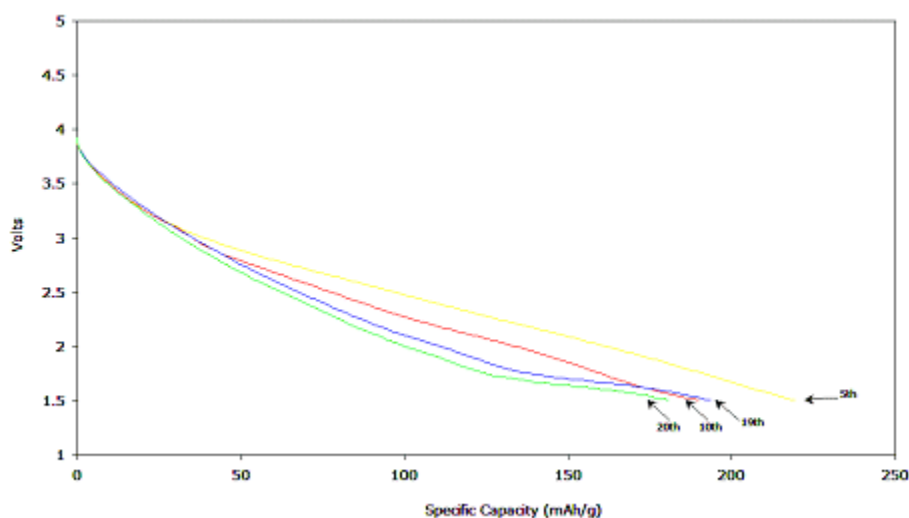


Figure 4. Discharge profile of $\text{Mg}_{0.2}\text{Cu}_{0.2}\text{MnO}_x$ for select cycles.

The discharge profile for $\text{Mg}_{0.2}\text{Cu}_{0.2}\text{MnO}_x$ at C/5 rate (or 0.67 mA/cm²) is shown in Figure 4. Both the capacity plot and the discharge curves show a slight increase in capacity between the 10th and 19th cycles. In addition, a minor deflection at ~1.7 V is observed for cycles 11 - 20, which is most prevalent for the 19th and 20th cycles. This possibly indicates more lithium intercalates around this potential than at any other potential, or that local structures in the amorphous material are experiencing a minor transformation upon Li-intercalation. This phenomenon is particularly interesting as it is not characteristic of the copper-doped manganese oxide reported by Xu et al. [9]. However, the cause of the reduced curvature at this potential is not understood at this time

Conclusion

Mg, Cu-doped amorphous manganese oxides have been successfully synthesized by using a cost efficient, environmentally acceptable, solution-based oxidation route at room temperature. Though 100% capacity retention is only maintained through 10 cycles, the cycling performance is drastically improved over pure amorphous manganese oxide and copper-doped amorphous manganese oxide. The absence of global phase transformation during repeated Li interaction / de-intercalation suggests the amorphous structure is stable. Better optimization of the dopant concentrations could yield materials with better performance and perfect capacity retention.

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