Vanadium-doped manganese oxides as cathode materials for rechargeable lithium batteries

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Abstract

Vanadium-doped manganese oxides meant for use as lithium intercalation cathode materials have been prepared by oxidation of Mn(II) precursors in the presence of V_2O_5 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, even after heating the material for 24 hours at 400 °C, there was no evidence of significant crystallization. The failure to crystallize indicates that the presence of vanadium stabilizes the high-energy amorphous structure. Electrochemical characterization of these cathode materials showed a specific capacity of 50-70 mAh/g and excellent capacity retention upon cycling.

Introduction

Transition metal oxides have been considered for electrode materials for many battery systems, including rechargeable (or secondary) lithium batteries. A typical lithium battery consists of a lithium anode, a transition metal oxide cathode, and an organic electrolyte containing lithium ions. It was once believed that the reaction of lithium metal and a transition metal oxide yielded lithium oxide due to reduction of the transition metal oxide. However, emf values were not consistent with thermodynamically expected values [1]. Studies of the expansion in volume of the transition metal oxide structure concluded that lithium was in fact intercalated into the transition metal oxide structure. This work led to further research on intercalation compounds. An intercalation compound, by definition, is a compound that undergoes little or no structural change as a result of the reaction, acting as a host for the other reacting species. Transition metal oxides have the ability to form intercalation hosts for lithium and for this reason have attracted enormous interest as cathodes for rechargeable lithium batteries.

Titanium disulfide was one of the first prototype cathodes for rechargeable lithium batteries. The reaction between lithium metal and titanium disulfide appears to be an ideal intercalation reaction. Through the insertion of up to 1.0 mole Li in 1.0 mole of TiS_2 , the structure remains stable. The structure maintains hexagonally close-packed sulfur sheets where sulfur is covalently bonded to titanium. This reduces electrostatic

cation repulsion allowing for higher intercalation capacity. The stability of the structure promotes excellent cycling performance as lithium is inserted and extracted from atomic vacancies with minimal crystal expansion [1]. However, TiS_2 retains a low energy density and insufficient voltage for advanced applications.

LiCoO₂ has also been found to have useful properties for lithium batteries. Although the parent compound, CoO_2 , possesses a hexagonal structure similar to TiS₂, lithiation causes phase transformation to a cubic close-packed structure. This transformation is unfavorable because the Li⁺ cations do not approach each other as closely as they do in TiS₂. Subsequent phase transformations limit further reduction of Co and decrease intercalation capacity. Hence, LiCoO₂ only maintains sufficient cycling performance through 0.5 Li intercalation / de-intercalation. However, voltages attained by LiCoO₂ have made it commercially successful in the Sony Li-ION cell [1]. Another disadvantage of lithium cobalt oxide is that it is toxic and too expensive for practical large-scale applications.

Manganese oxides have been investigated because of their low cost and nontoxicity. Many crystalline, amorphous, and aerogel forms of manganese oxides have been studied; each one has advantages and disadvantages. Spinel structures of manganese oxides have particularly been investigated for battery applications, but so far they have exhibited lower intercalation capacity and poorer cycling performance than LiCoO₂. At voltages of 4 V, cubic spinel Li_xMn₂O₄ can sufficiently cycle 0.4 Li. Though cubic spinel may intercalate up to 1.0 Li at 4 V with minimal isotropic expansion of the crystal lattice, dissolution of Mn^{3+} and oxidation of electrolyte causes gradual capacity loss upon cycling. Upon intercalation of more than 1.0 Li, cell potential drops to 3 V and the cubic symmetry converts to a tetragonal symmetry, which causes a large increase in the volume of the crystal lattice and degrades cycling performance [2].

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 and may serve as high performance cathodes. Synthesis of amorphous manganese oxides has been the focus of a few recent reports [3-5] and capacities in the range of 160-250 mAh/g have been attained. Remarkably, capacities greater than 400 mAh/g were reported by Xu et al for an amorphous manganese dioxide [3]. Cycling performance, however, remains an issue for these high capacity amorphous compounds. Even though the structure of these amorphous compounds is not likely to undergo any global phase transformations during repeated intercalation / de-intercalation, the local structure may undergo gradual changes upon cycling [6]. Such local structure changes may prevent good capacity retention upon insertion and extraction of lithium.

Dopants have been utilized to improve cycling performance and stabilize electrochemically favorable structures. Dopants may be able to improve capacity retention upon cycling if phase transformation is suppressed and volume expansion becomes isotropic and minimized upon lithium insertion. [7]. Potassium has been observed to act as a phase-transforming suppressant, but capacity fading and phase conversion have been found to occur at higher current rates [8]. Vanadium-doping has also been studied recently for a potential pillaring effect in crystalline structures. Most V-doped compounds for battery applications have been synthesized using hydrothermal and sol-gel techniques.

We discuss a novel solution-based oxidation route to the synthesis of amorphous manganese oxides with varying concentrations of vanadium. The synthesis route yields materials with capacity retention upon cycling that is better than that of pure amorphous manganese oxides. 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 vanadium-doping on the electrochemical properties of amorphous manganese oxides as lithium intercalation hosts.

Experimental

Two novel synthesis methods were attempted in order to prepare vanadium-doped manganese oxides. Redox reactions in aqueous solutions were performed to yield powder precipitates of manganese oxide doped with vanadium [9].

Initially, 1 M MnCl₂ o4H₂0 and 1 M VCl₃ were added to a solution of 1600 mL of de-ionized water, 1 M NaOCl oxidant, and 1 M NaOH having pH ~11.6 to precipitate a brown fine powder at room temperature. The solution was stirred for 1.5 h in an acidic medium of pH ~3.5. 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 or vanadium, additions of NaOH, HCl, and NaOCl were made to the supernatant. Additions of these reagents helped to determine the completion of the reaction and necessary adjustments to the concentrations of the reagents used in the synthesis.

The second synthesis method was similar to the initial solution-based synthesis. 1 M MnCl₂ o4H₂0 was ultra-sonicated with a 0.005 M V₂O₅ solution and added to 1600 mL of a solution made from de-ionized water, 1 M NaOCl, and enough 1 M NaOH to give a pH of ~12.1. We maintained the combined solution at a pH of ~11.5 as it was stirred for 24 h. The resultant black precipitate of fine particles underwent the same treatment as described above after completion of stirring. The concentrations of the reagents used in the syntheses are shown in Table 1. X-ray powder diffraction (XRD) measurements were collected with a Siemens Diffractometer® using Cu Ka radiation ($\lambda = 1.5418$ Å) for structure analysis.

For electrochemical studies, the active material was mixed with 30% carbon black and 10% PTFE powder by weight and dry pressed at 1 metric ton for 30 min. Samples were 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/dimethoxyethane with 1:1 ratio was used 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

The initial synthesis with VCl₃ was unsuccessful in doping manganese oxide with vanadium. Similar electrochemical properties to pure manganese oxide, displayed in Figure 1, indicated that vanadium was not significantly present in the sample and therefore had no effect on the electrochemical properties of the sample . Precipitation of VCl₃ upon treatment of the supernatant also showed evidence that vanadium was not appreciably incorporated.



Figure 1: Capacity performance of sample synthesized with VCl₃.

Treatment of the supernatant and electrochemical testing (discussed below) in later syntheses indicated successful incorporation of vanadium from the V_2O_5 source into the manganese oxide. V_2O_5 , which is soluble at higher pH values and insoluble in acidic medium, was undetectable as HCl was added to the supernatant. Additionally, no manganese was detected either. The synthesis used allows good control of dopant content in the synthesized material and is less expensive, which is attractive for largescale applications. Initially when VMn1 (Table 1) was synthesized, a purple color from the supernatant indicated a presence of permanganate ions owing to excess oxidizing agent (NaOCl) being used for the synthesis. VMn3 was synthesized with half the amount of oxidant resulting in a lighter purple color of supernatant. However, particle size and flocculation became a concern in aqueous solution of pH between 7 and 8. In order to promote dispersion and eliminate excess permanganate ions, samples VMn2 and VMn4 were synthesized with more NaOH and less NaOCl.

| Sample | Mn | V | NaOH | NaOCl | Mn/V | Mn/Na |
|--------|----|------|------|-------|-------|--------|
| VMn1 | 1 | 0.4 | 1.75 | 5.0 | 2.5/1 | 1/6.75 |
| VMn2 | 1 | 0.2 | 4.0 | 2.0 | 5/1 | 1/6.0 |
| VMn3 | 1 | 0.1 | 1.15 | 2.5 | 10/1 | 1/3.65 |
| VMn4 | 1 | 0.05 | 4.0 | 2.0 | 20/1 | 1/6.0 |

Table 1: Initial concentrations (M) of constituentsused in synthesis by molar ratio.

Figure 2 shows X-ray diffraction patterns for pure amorphous manganese oxide, vanadium doped manganese oxide, and V-doped manganese oxide heated at 400 °C for 24 h in air. All the vanadium-doped manganese oxide samples exhibit a similar amorphous structure resembling pure amorphous manganese oxide [6]. The XRD pattern appears similar to those of the birnessite group of phyllomanganates, which are layered compounds with an inter-layer spacing of 7Å [5]. The weak peaks at 37° and 66° correspond to the Mn⁺⁴-O spacing in an octahedral arrangement, similar to amorphous manganese oxides reported by Leroux et al [10] and Palos et al [11]. Therefore, this XRD pattern suggests a very weakly layer-like, amorphous structure.

Figure 2: X-ray Diffraction data.



XRD taken after the V-doped manganese oxides were heated for 24 hours at 400 °C showed no evidence of crystallization. The failure to crystallize suggests that the vanadium-doped samples are very stable as an amorphous structure and that the addition of vanadium significantly raises the energy barrier towards crystallization. In contrast, layered Li_xMnO_2 readily converts to spinel LiMnO_2 at 400 °C as do many other manganese oxides [8]. It is unusual for high energy amorphous structures to remain intact after exposure to temperatures as high as 400 °C. Though the bulk analysis is inconclusive in identifying variations in the three amorphous structures in Figure 2, there are some differences observed in electrochemical behavior.

Electrochemical data for pure amorphous manganese oxide and for the vanadiumdoped samples are shown with in Figure 3. Through 40 cycles, vanadium doping has dramatically improved capacity retention compared to that of the pure manganese oxide. The enhancement of the capacity retention may be due to improved structural stability, which is also indicated by XRD analysis. However, the capacity of the samples is dramatically lower than that of the pure manganese oxide. The decreased capacity suggests that vanadium blocks the intercalation pathways that lithium must traverse. Specific capacity reduction was also reported by P. Liu et al. as the Mn/V ratio in synthesis was increased [12].



Figure 3: Capacity performance of samples synthesized with V-Doped MnO₂ and pure MnO₂.

Discharge profiles for the vanadium-doped samples at C/5 rate (or 0.67 mA/cm2) are shown in Figure 4. Each vanadium-doped sample maintained an open-circuit voltage (OCV) of ~3.3 V. All the profiles show a continuously sloping curve, which indicates a single phase throughout intercalation / de-intercalation of Li. The profiles show a very slight positive slope change around 3 V, which may be related to the Jahn-Teller effect causing distortion of the $[MnO_6]^9$ octahedron in the structure. All the samples show a slight capacity fading in the initial cycles, but excellent retention in the later ones. Over a range of 40 cycles, fading for the final N cycles was as follows:, VMn1 0.06% for N=20; VMn2 0.03% for N=30 cycles; VMn3 0.01% for N=30 cycles, and VMn4 0.07% for N=27. Pure amorphous manganese oxide shows much higher average capacity fading of >1% per cycle [6]. The lessened fading in the doped compounds indicates their greater kinetic stability. VMn3 also shows slightly higher specific capacity than the other samples. The increase in specific capacity might be the effect of a possible lower sodium concentration for that sample. Referring to Table 1, VMn3 has the lowest sodium concentration in synthesis.



Figure 4: Discharge Profiles of a) VMn1 b) VMn2 c) VMn3 d) VMn4.

Figures 5 and 6 show electrochemical data at C/5 rate for selected VMnx samples heated for 24 hours at 400 °C. Though only the first 10 cycles are shown, there was significant variation from the unheated samples in electrochemical behavior. After heating, VMn3 showed the most improvement in specific capacity, followed by VMn4 and VMn2 respectively. After heating, VMn3 attained a specific capacity over 100 mAh/g. This capacity may be the effect of oxidation of manganese in the compounds. Higher oxidation states of manganese should improve intercalation because more lithium must react in order to reduce manganese to a 2⁺ oxidation state. Another possibility is that slight rearrangements at the sites occupied by vanadium may have opened some intercalation pathways for lithium ions to pass. Although capacity improved for all three samples, only VMn4 showed higher capacity retention upon cycling. VMn2, VMn3 and VMn4 showed average capacity fading of 1.0%, 1.2%, and 0.03% per cycle through ten to fifteen cycles respectively. This suggests that local structure changes may have evolved due to heating. The remarkable improvement in capacity retention for VMn4 may be due to structural relaxations as a result of heating.



Figure 5: Cycling Performance for V-Doped MnO₂ after heating for 24 h at 400 °C.





Similar to the unheated samples, all the profiles for the heated samples in Figure 6 show a continuously sloping curve, which indicates a single phase throughout the electrochemical reaction. Each heated sample had an OCV of ~3.4 V. All three profiles of the heated samples show an increased positive slope change just below 3 V. Dramatically sharper slope changes have been observed with the crystalline spinel and layered-structure manganese oxides due to the Jahn-Teller effect when close to 50% of the manganese attain 3+ oxidation state. [13, 14].

All the electrochemical test samples retained a charge coefficient (ratio of charge capacity to discharge capacity) at nearly 100% upon cycling (Fig. 7). The relative

constancy of the ratio indicates that undesirable reactions, such as extraction of vanadium/sodium from the structure, do not occur. This further indicates the stability of the structure which is suggested by XRD and the improved capacity retention upon cycling.





Conclusion

Vanadium-doped amorphous manganese oxides have been successfully synthesized by using a cost efficient, environmentally acceptable, solution-based oxidation route at room temperature. Though their specific capacity is substantially lower, the V-doped amorphous manganese oxides exhibit significantly improved cycling performance over pure amorphous manganese oxide. The absence of phase transformation during repeated Li interaction / de-intercalation suggests the amorphous structure is very stable. Notably, further stability is indicated by lack of any evidence of crystallization after heating up to 400 °C. The variation in electrochemical behavior among the samples with varying vanadium content suggests there may exist an optimal concentration, attainable in the laboratory, at which capacity and capacity retention upon cycling are maximized.

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