Modulating Conductivity in Materials by Design: Battery Relevant Study of Ag^+ on the Exposed Surface of $Ag_{1.13}Mn_8O_{16}$ Nanowires

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Modulating Conductivity in Materials by Design: Battery Relevant Study of Ag^+ on the Exposed Surface of $Ag_{1.13}Mn_8O_{16}$ Nanowires

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Design and development of novel materials can have a profound impact on the electrochemical properties of energy storage systems. Silver ion when electrochemically reduced to generate conductive silver metal *in-situ* can provide enhanced conductivity in electrochemical energy storage systems. In this research, Ag_2O surface modified silver hollandite ($Ag_xMn_8O_{16}$, α-MnO_2 structure) has been successfully synthesized and its physical, chemical, and electrochemical properties have been studied. The electrochemical tests indicate a higher functional capacity can be delivered with higher Ag_2O loading, consistent with an increase in the electric conductivity of the material. This result demonstrates the ability to modulate conductivity in materials by design.

Introduction

Driven by the increasing demand for high energy and power density for various modern electrical devices, design and development of new battery systems is necessary. Lithium-ion batteries are often the systems of choice for many applications, with the ability to offer high energy density.(1) Important characteristics that are needed for a successful cathode include containing readily reducible/oxidizable ions (often transition metals), being able to react with lithium reversibly and rapidly, and having a high capacity, and high voltage to achieve high specific energy. It is also important that the material is a good conductor of electricity. The electrode system within a battery must allow both ion and electron transport, requiring the materials that make up the system to be both good ionic and electrical conductors.(2) Significant improvements in functional capacity may be achieved through reduction of internal resistance.

Hollandite, or α-MnO_2, is structured with eight MnO_6 octahedra linked together 2 x 2 to form tunnels, approximately 4.6 nm in diameter, which usually contain alkali or alkaline earth metals

in the center. This tunnel structure allows for easy insertion and deinsertion of ions and small molecules, which makes the hollandite structured material useful for sorbent and catalysis applications.(3, 4) However, hollandite is only semi-conducting at best. To improve the conductivity of hollandite, dopants, conductive additives, or cations which produce conductive matrices have been added. Specifically, silver hollandite, which is hollandite with an electrochemically active center of Ag^+, has been identified to be a material of interest for electrochemical energy storage.(5, 6) The intra-tunnel Ag^+ content (x in $Ag_xMn_8O_{16}$) has been varied and tested to see its effects on electrochemical performance where a concomitant decrease in crystallite size and silver content was observed. A higher capacity was observed in the case of the smaller crystallite size material with lower silver content.(7, 8) Thus, lower silver content $Ag_{1.13}Mn_8O_{16}$ was identified as a material of interest for this study.

To bring us closer to the goal of wiring every electroactive particle,(9) the approach studied here was encapsulating silver hollandite ($Ag_{1.13}Mn_8O_{16}$) nanowires with a thin coating of silver oxide (Ag_2O). As the electrons enter the $Ag_{1.13}Mn_8O_{16}{\cdot}aAg_2O$ cathode, the theory tested here is that they would reduce the Ag_2O coatings to create silver metal on the surface of the hollandite nanorods. A series of samples with varying Ag_2O:$Ag_{1.13}Mn_8O_{16}$ ratios was prepared, characterized, and electrochemically tested to learn about the effect of surface silver content on electrochemical performance.

Experimental

Synthesis procedure

Silver hollandite was synthesized using a previously reported method.(7) The silver hollandite ($Ag_xMn_8O_{16-y}$) was coated with silver oxide where a silver hollandite suspension in aqueous $AgNO_3$ solution was treated with NaOH. Three samples with molar ratios of 2:1, 1:1, and 1:2 silver hollandite to silver oxide were prepared.(10)

Materials characterization

X-ray powder diffraction (XRD) was used to identify the crystalline structure and size of the as-synthesized materials. For search match analysis, MDI-JADE was used with ICDD and NIST databases. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted using an SDT Q600 TA instrument. For Fourier transform infrared spectroscopy (FT-IR), a Thermo Scientific Nicolet iS10 spectrophotometer with attenuated total reflectance accessory (ATR) was used at a wave number range of 4000 cm^{-1} to 500 cm^{-1}. Inductively coupled plasma atomic emission spectroscopy (ICP-OES) was used to quantify the Ag and Mn content. Transmission electron microscopy (TEM) results were collected using a JEOL JEM 1400 equipped with a Gatan CCD camera.

Electrochemical characterization

Electrodes of the synthesized materials pellets were prepared either as pure materials or as composites consisting of 85:10:5 (mass ratio) of active material: carbon: PVDF. Coin cells were assembled in an Argon filled glove box with Lithium metal anodes and 1 M $LiPF_6$ 70/30

dimethyl carbonate/ethylene carbonate electrolyte. A current density of 1 mA/g was used for discharge, and interrupted every 1% of theoretical capacity three times and every 5% for the remainder of discharge. The AC impedance was recorded at open circuit voltage and analyzed using Z-view software.

Results and Discussion

X-ray diffraction results of the Ag^+ treated silver hollandite samples are shown in Figure 1(a). For silver hollandite, all peaks can be indexed to the reference pattern (JCPDS card No. 97-006-015). When Ag_2O content is low (a=0.25 and 0.63), XRD could not readily discern the peaks from the phase.(11) However, when the Ag_2O amount reaches a=1.43, reflections at 34◦, 37◦ and 56◦ 2θ can be identified as cubic Ag_2O(5). The Rietveld refinement of the structure shows lattice parameters a=b= 9.784 and c=2.8616 which are consistent with the previous reports.(8) Also, a phase fraction of 17% has been achieved for Ag_2O content. To further confirm the Ag_2O phase, FTIR spectra have been recorded, Figure 2(b). As the Ag_2O amount increases, the FTIR spectra continue to demonstrate the silver hollandite peaks while the intensity of peaks at 1380 cm^{-1} relating to silver oxide increase. Thus, both XRD and FTIR data indicate that the silver hollandite structure remains intact with the synthetic procedure. Also, the ability to tailor the Ag_2O amount was confirmed.

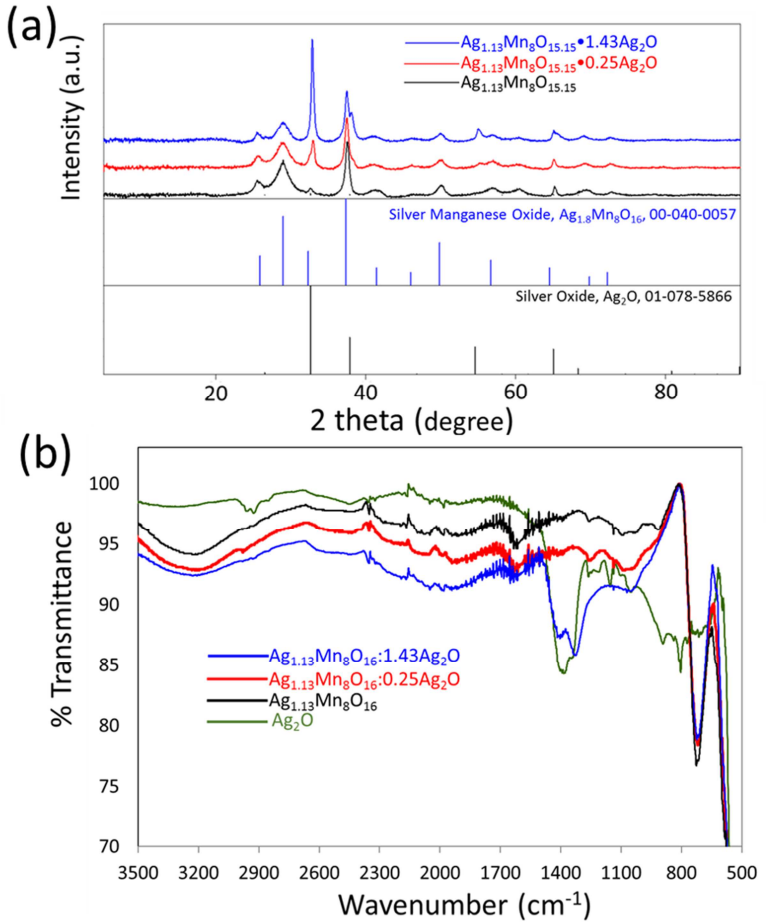

Figure 1. (a) XRD and (b) FTIR of silver hollandite and silver oxide modified silver hollandite

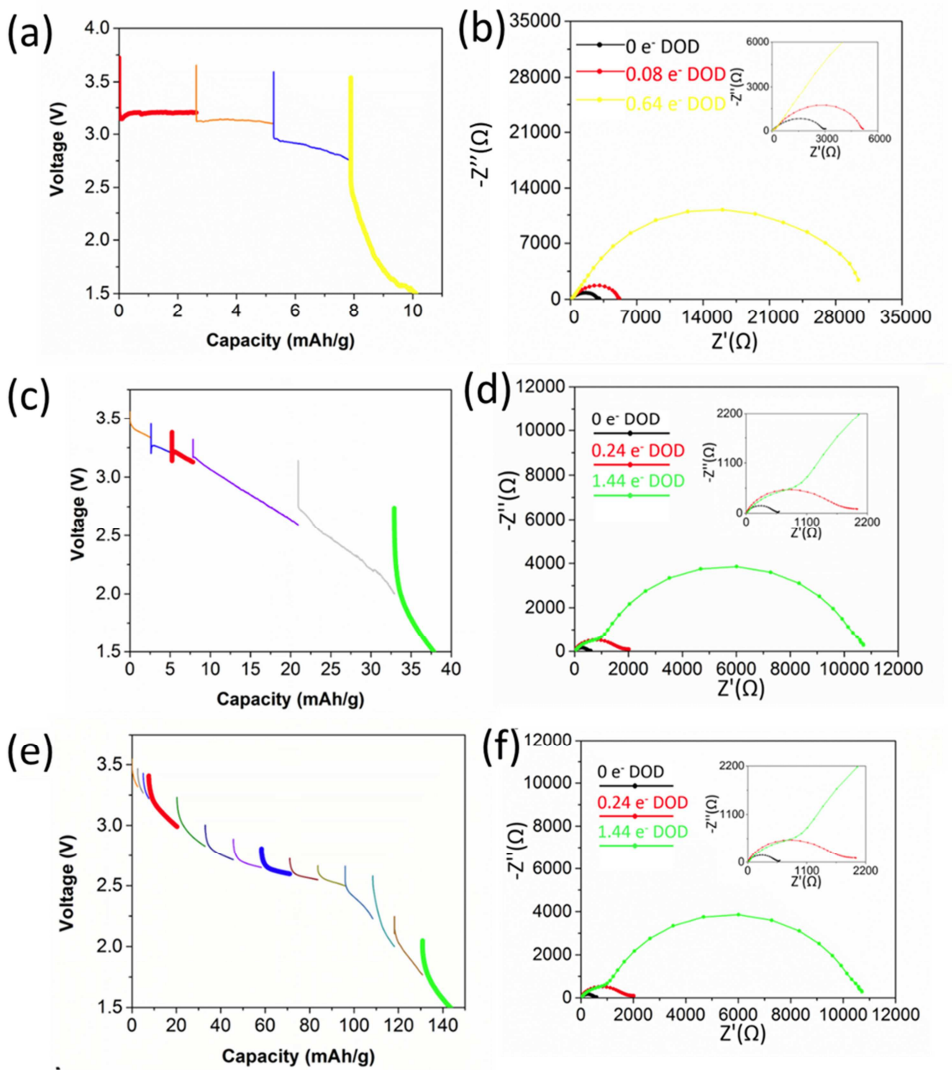

Figure 2. Voltage of (a) $Ag_{1.13}Mn_8O_{15.15}$, (c) $Ag_{1.13}Mn_8O_{15.15}$•$0.25Ag_2O$ and (e) $Ag_{1.13}Mn_8O_{15.15}$•$1.43Ag_2O$ electrochemical cells discharged under galvanotatic control. Nyquist plots of (b) $Ag_{1.13}Mn_8O_{15.15}$, (d) $Ag_{1.13}Mn_8O_{15.15}$•$0.25Ag_2O$ and (f) $Ag_{1.13}Mn_8O_{15.15}$•$1.43Ag_2O$ corresponding to (a), (c) and (e).

Electrodes of pure hollandite materials ($Ag_{1.13}Mn_8O_{15.15}$) were reduced in coin cells and the discharge profile is shown in Figure 2(a). The sample showed significant decrease in their voltages upon initial reduction and only delivered a capacity of 8 mAh/g above 2.0V. This observation can be attributed to limited electronic conductivity, as shown in Figure 2(b), where an impedance of ~30000 Ω was noted when the voltage reached 2.0V. However, for electrodes with a small amount of Ag_2O coating (a=0.25), sloping voltage profiles were observed, Figure 2(c). A capacity of 30 mAh/g was delivered above 2.0 V compared to 8 mAh/g for pure hollandite. When the Ag_2O amount was increased to a=1.43, a capacity of 121 mAh/g was observed, Figure 2(d). The higher capacity can be attributed to significantly lower impedance for the Ag_2O coated material (Figure 2(e)), consistent with the appearance of Ag metal upon electrochemical reduction by XRD, Figure 3.

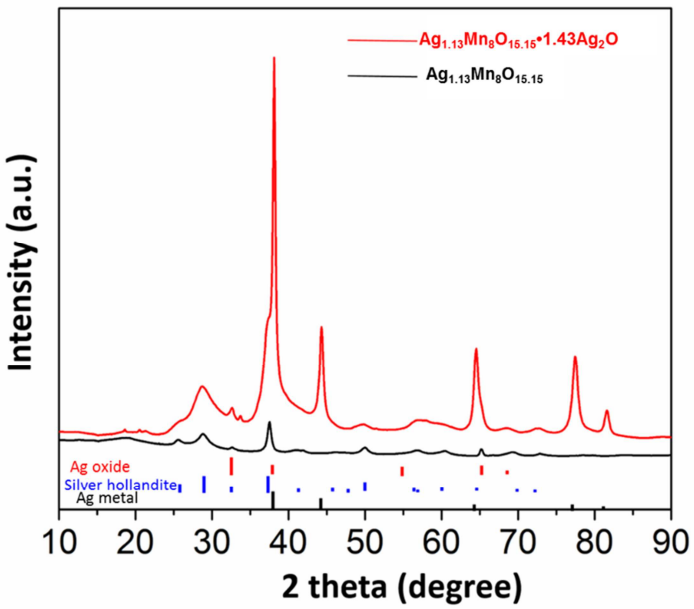

Figure 3. XRD of $Ag_{1.13}Mn_8O_{15.15}$•1.43Ag_2O after 1st discharge

Conclusion

In this research, Ag_2O modified silver hollandite has been successfully synthesized and the electrochemical properties have been studied. ICP-OES was used to identify the total silver content in the samples. Both XRD and FTIR indicated the formation of cubic Ag_2O on the surface of the tunnel structured manganese oxide materials. Electrochemical evaluation showed higher capacities with more Ag_2O present with no carbon used as a conductive additive. For carbon containing electrodes, both Ag_2O modified and unmodified materials delivered the same capacity at low discharge rate, but a much higher capacity by the Ag_2O modified material when the discharge rate was high. These results have shown the important role of electrical conductivity in impacting the electrochemical properties of hollandite materials.

Acknowledgments

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