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Bimetallic or trimetallic materials with structural metal centers based on Mn, Fe or V were investigated under this project. These metal centers are the focus of this research as they have high earth abundance and have each shown success as cathode materials in lithium batteries. Silver ion, Ag^+ , was initially selected as the displacement material as reduction of this center should result in increased conductivity as Ag^0 metal particles are formed in-situ upon electrochemical reduction. The in-situ formation of metal nanoparticles upon electrochemical reduction has been previously noted, and more recently, we have investigated the resulting increase in conductivity. Layered materials as well as materials with tunnel or channel type structures were selected. Layered materials are of interest as they can provide 2-dimensional ion mobility. Tunnel or channel structures are also of interest as they provide a rigid framework that should remain stable over many discharge/charge cycles. We describe below some examples of materials we have synthesized that demonstrate promising electrochemistry.

Silver Based Materials

Silver Manganese Oxide. The silver cation in $\text{Ag}_x\text{Mn}_y\text{O}_z$ hollandite-type structures is located in a regular position within the manganese oxide tunnel. Due to the porous open tunnel structure of the hollandite manganese oxides, the Ag^+ can readily migrate within the tunnel without disturbing the manganese oxide structure (Figure 1). Co-PI K. Takeuchi has achieved remarkable results associated with modification of the $\text{Ag}_x\text{Mn}_y\text{O}_z$ synthesis parameters, a material here to fore challenging to prepare at high purity. A new synthesis method was

developed utilizing ambient pressure reflux conditions, and this process was successfully scaled up to produce gram quantities of material. The added advantage of the reflux method is the ready possibility for further scale up to generate adequate supply for future studies.

The $\text{Ag}_x\text{Mn}_y\text{O}_z$ material was characterized by x-ray diffraction (XRD) and inductively coupled plasma – optical emission spectrometry (ICP-OES). XRD was consistent with previous literature preparations of the material, showing a hollandite-type manganese oxide structure. ICP-OES showed the materials to be free of residual K^+ from the starting material, a complication which can occur in the synthesis of hollandite materials.

We have obtained encouraging preliminary results associated with modification of the Ag:Mn ratio of the $\text{Ag}_x\text{Mn}_y\text{O}_z$ material. Using his novel reflux method for synthesis of $\text{Ag}_x\text{Mn}_8\text{O}_{16}$, a series of manganese oxide materials with differing Ag:Mn ratios and varying crystallite sizes was successfully synthesized (Figure 2). XRD suggested that the silver was fully incorporated within the manganese oxide structures, with no evidence of residual unreacted starting material.

ICP-OES verified the Ag:Mn ratios covered the desired range where x in $\text{Ag}_x\text{Mn}_8\text{O}_{16}$ was $1.0 \leq x \leq 1.8$. $\text{Ag}_x\text{Mn}_y\text{O}_z$ electrodes were prepared and tested in a 3-electrode configuration, with the $\text{Ag}_x\text{Mn}_y\text{O}_z$

working electrode, lithium pseudo-reference electrode, and lithium common electrode. Based on the SSRV data, the $\text{Ag}_x\text{Mn}_y\text{O}_z$ showed reversible electrochemical behavior, demonstrating good promise as a future electrode material for secondary lithium-ion batteries (Figure 3).

Discharge of $\text{Li}/\text{Ag}_x\text{Mn}_8\text{O}_{16}$ cells demonstrated capacity $\sim 180 \text{ mAh/g}$ (Figure 4). Cycling tests showed good capacity retention for cycles 3 – 30, after a larger 25% drop in discharge capacity between the 1st and 2nd cycles.

Silver Ferrite (AgFeO_2). The delafossite (ABO_2) structure consists of close-packed double layers of edge-sharing BO_6 octahedra with monovalent A^+ ions positioned between the layers. Despite their layered structures, often desirable for ion insertion, delafossites have remained relatively unexplored for electrochemical applications. We recently reported the first investigation of the electrochemical properties of silver ferrite (AgFeO_2), including its use as a cathode material in secondary lithium based batteries. The only prior reported use of a bimetallic delafossite as a battery material was for a AgNiO_2 cathode in zinc based alkaline batteries.

Silver ferrite (AgFeO_2) possesses the α -type delafossite structure with rhombohedral type stacking (3R-polytype), consisting of close-packed

double layers of FeO_6 octahedra with monovalent Ag^+ ions positioned between the layers (Figure 5). Silver ferrite has been one of the least studied members of the delafossite family, where available information on silver ferrite to date was limited to synthetic studies, crystallographic studies, and assessments of its optical, electronic, and magnetic properties. We anticipated that the O-Fe-O layered structure would provide a framework for Li^+ insertion and de-insertion making AgFeO_2 a potentially electrochemically rechargeable material. In addition, we anticipated that the presence of the silver ion would provide increased conductivity within the electrode matrix on reduction to silver metal as well as contributing to energy content. Cyclic voltammetry data showed the material to be electrochemically active. SEM, EDS, and XRD revealed Ag^0 metal formation upon discharge, consistent with an electrochemical reduction-displacement mechanism. While the AgFeO_2 material exhibited larger voltage recovery during the first 0.1 electron equivalent of reduction, the polarization throughout the remaining discharge was small (Figure 6). After cycle one, the material maintained consistent capacity over 50 discharge-charge cycles under a C/5 rate.

Silver vanadium phosphorous oxide ($\text{Ag}_{0.43}\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$). The silver vanadium phosphorous oxide studied here, $\text{Ag}_{0.43}\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, has a layered structure, with Ag^+ and H_2O between the layers (Figure 7). The material was prepared and fully characterized.

Figure 5. Structure of AgFeO_2

Figure 6. Polarization data for $\text{Li} / \text{AgFeO}_2$ cells

The electrochemistry of $\text{Ag}_{0.48}\text{VOPO}_4 \cdot 1.9\text{H}_2\text{O}$ was examined by cyclic voltammetry using lithium metal reference and auxiliary electrodes in an experimental cell. After the initial discharge, the material displayed reversible electrochemistry supporting the concept that reversible electrochemistry is achievable after the reduction of the displacement material (Figure 8). Thus, promising results have been obtained from several compounds in this class of materials. The results support the further investigation of the classes of bimetallic and trimetallic electrochemical displacement materials defined as: $M_wM'_x\text{O}_z$, $M_wM'_x\text{OP}_y\text{O}_z$, and $M_wM'_x\text{P}_y\text{O}_z$.

Mechanistic Insights

Nanocrystalline materials are desirable for electrochemical energy storage applications, as the high surface area enables fast ion diffusion and rapid electron transfer. However, structural and coordination environment characterization using conventional methods can be challenging, making it difficult to monitor structural changes upon lithiation of nanocrystalline materials. X-ray absorption spectroscopy methods such as x-ray absorption fine structure (XAFS), x-ray absorption near edge structure (XANES), and extended x-ray absorption fine structure (EXAFS) measurements can be powerful tools for mechanistic interrogation. We have employed these methods for analysis of $\text{Ag}_2\text{VO}_2\text{PO}_4$ as a function of discharge.

Using a combination of V K-, V L-, Ag K-, and O K-edge x-ray absorption fine structure (XAFS) spectroscopy, with XANES and EXAFS measurements, we determined the local vanadium and silver oxidation states, local coordination geometry, and stoichiometry for $\text{Ag}_2\text{VO}_2\text{PO}_4$ samples with varying extents of lithiation. By comparing the peak positions of

discharged $\text{Ag}_2\text{VO}_2\text{PO}_4$ samples with known binary vanadium oxide standards, a vanadium oxidation state of 4.64 ± 0.18 was deduced for the sample at 25% depth of discharge (Figure 9). During the initial two discharge steps, the contributions from Ag^0 were determined to be $31 \pm 6\%$ at 25% DOD and $59 \pm 5\%$ at 50% DOD. These results were significant as they confirmed that while reduction of Ag^+ was the predominant initial process upon discharge of $\text{Ag}_2\text{VO}_2\text{PO}_4$, some reduction of V^{5+} and V^{4+} was also occurring in parallel.

Papers Acknowledging DOE Support

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7. Yau, Shali Z.; Farley, Katie E.; Marschilok, Amy C.; Takeuchi, Esther S.; Takeuchi, Kenneth J. "Synthesis and electrochemistry of nanocrystalline iron and manganese oxide materials." *Electrochemical Society Transactions*. **in press**.
8. Marschilok, Amy C.; Kim, Young Jin; Takeuchi, Kenneth J.; Takeuchi, Esther S. "In situ generation of electrically conductive nanoparticles in bimetallic phosphate materials for high power batteries." *Electrochemical Society Transactions*. **in press**.

9. Marschilok, Amy C.; Schaffer, Corey P.; Takeuchi, Kenneth J.; Takeuchi, Esther S. "Carbon nanotube-metal oxide composite electrodes for secondary lithium based batteries." *in press*.

Presentations acknowledging DOE support

1. Shali Zhu, Amy C. Marschilok, Esther S. Takeuchi, Kenneth J. Takeuchi. "Nanocrystalline magnetite synthesis and electrochemistry," 238th National Meeting of the American Chemical Society, Washington, D.C., August 17, 2009.
2. E. S. Takeuchi, "Broad based challenges for advanced battery implementation," Musselman Lecture Series, Gettysburg College, Gettysburg, PA, November 12-14, 2009. *Invited lecture*.
3. E. S. Takeuchi, "Broad based challenges for advanced battery implementation," Musselman Lecture Series, Gettysburg College, Gettysburg, PA, November 12-14, 2009. *Invited lecture*.
4. E. S. Takeuchi, "Meeting future energy storage needs: Navigating the science and technology boundary," Chemical Sciences Roundtable, National Academy of Science, Washington, DC, February 3, 2010. *Invited lecture*.
5. Chia-Ying Lee, Aditya Subramanian, Kenneth J. Takeuchi, Amy C. Marschilok, Esther S. Takeuchi. "Investigation of vanadium oxides prepared by ion exchange," 217th Electrochemical Society, Vancouver, Canada, April 26, 2010.
6. Shali Zhu, Amy C. Marschilok, Esther S. Takeuchi, Kenneth J. Takeuchi, "#436: Novel synthesis and electrochemistry of silver hollandite," 15th International Meeting on Lithium Batteries, IMLB, Montreal, Canada, June 29, 2010.
7. Esther S. Takeuchi, Chia-Ying Lee, Young Jin Kim, Aditya Subramanian, Amy C. Marschilok, Kenneth J. Takeuchi. "#309: Opportunities for multiple electron transfer in cathode materials," 240th American Chemical Society National Meeting, Boston, Massachusetts, August 22, 2010.
8. Kenneth J. Takeuchi, Shali Zhu, Amy C. Marschilok, Esther S. Takeuchi. "#220: New synthetic strategies towards lower cost, sustainable energy materials," 240th American Chemical Society National Meeting, Boston, Massachusetts, August 22, 2010.
9. Kenneth J. Takeuchi, Shali Zhu, Amy C. Marschilok, Esther S. Takeuchi. "#352: Synthesis, characterization and electrochemical properties of silver hollandite," 240th American Chemical Society National Meeting, Boston, Massachusetts, August 23, 2010. *Invited conference presentation*.
10. Shali Zhu, Amy C. Marschilok, Esther S. Takeuchi, Kenneth J. Takeuchi. "#357: Synthesis, characterization and electrochemical properties of magnetite," 240th American Chemical Society National Meeting, Boston, Massachusetts, August 23, 2010. *Invited conference presentation*.

11. Esther S. Takeuchi, Amy C. Marschilok, Kenneth J. Takeuchi. "Challenges in battery implementation," 219th Electrochemical Society Meeting, Montreal, Canada, May 2, 2011.
12. Chia Ying Lee, Aditya Subramanian, Amy C. Marschilok, Kenneth J. Takeuchi, Esther S. Takeuchi. "#552: Exploration of novel metal oxide / carbon nanotube papers as composite electrodes," 218th Electrochemical Society, Las Vegas, Nevada, October 14, 2010.
13. E. S. Takeuchi, "Vanadium based cathodes for lithium batteries," Energy Frontier Research Center Lecture Series, Cornell University, Ithaca, NY, December 3, 2010. *Invited lecture*.
14. E. S. Takeuchi, "Broad based challenges for battery implementation," IGERT: Rutgers University, State University of New Jersey, New Brunswick, NJ, September 23, 2010. *Invited lecture*.
15. E. S. Takeuchi, "Vanadium based cathodes for lithium batteries," Stony Brook University Lecture Series, Stony Brook, NY, December 12, 2010. *Invited lecture*.
16. E. S. Takeuchi, "Vanadium based cathodes for lithium batteries," Brookhaven National Laboratory Lecture Series, Brookhaven National Laboratory, Long Island, NY, December 14, 2010. *Invited lecture*.
17. E. S. Takeuchi, "Broad Based Challenges in Battery Implementation," NY BEST Annual Conference, NY BEST, Albany, NY, March 9, 2011. *Invited conference presentation*.
18. E. S. Takeuchi, "Bimetallic cathodes for lithium based batteries," Frontiers in Materials Science Seminar Series, Pacific Northwest National Laboratory, Richmond, WA, July 2011. *Invited lecture*.
19. E. S. Takeuchi, "Nanoscope dimensional control of active materials: Impact on electrochemistry," Beyond Lithium Ion Conference, Pacific Northwest National Laboratory, Richmond, WA, July 2011. *Invited conference presentation*.
20. E. S. Takeuchi, A. C Marschilok, K. J. Takeuchi. "#182: Material Strategies for high power, high energy density lithium based batteries," 220th Electrochemical Society Meeting, Boston, MA, October 9, 2011.
21. E. S. Takeuchi, A. C Marschilok, K. J. Takeuchi. "#281: In-situ generation of electrically conductive nanoparticles in bimetallic phosphate materials for high power lithium batteries," 220th Electrochemical Society Meeting, Boston, MA, October 12, 2011.
22. K. J. Takeuchi, A. C Marschilok, E. S. Takeuchi. "#620: Synthesis and electrochemistry of nanocrystalline iron and manganese oxide materials," 220th Electrochemical Society Meeting, Boston, MA, October 12, 2011.
23. Katie E. Farley, Amy C. Marschilok, Esther S. Takeuchi, Kenneth J. Takeuchi. "Synthesis and Electrochemistry of Silver Ferrite," New York Battery and Energy Storage Technology Consortium (NY BEST), Rochester, NY, November 15, 2011.

24. Chia-Ying Lee, Amy C. Marschilok, Kenneth J. Takeuchi, Esther S. Takeuchi. "Carbon Nanotube Substrate Electrodes for Lightweight, Long-life Rechargeable Batteries," New York Battery and Energy Storage Technology Consortium (NY BEST), Rochester, NY, November 15, 2011.
25. Young Jin Kim, Amy C. Marschilok, Kenneth J. Takeuchi, Esther S. Takeuchi. "Ag_xVOPO₄: New Cathode Material for Lithium Batteries Powering Implantable Medical Devices," New York Battery and Energy Storage Technology Consortium (NY BEST), Rochester, NY, November 15, 2011.
26. Esther S. Takeuchi, "Broad Based Challenges in Battery Implementation," New York Battery and Energy Storage Technology Consortium (NY BEST), Rochester, NY, November 15, 2011. *Invited conference presentation.*