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Impact of Multifunctional Bimetallic Materials on Lithium Battery Electrochemistry

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Conspectus

Electric energy storage devices such as batteries are complex systems comprised of a variety of materials with each playing separate yet interactive roles, complicated by length scale interactions occurring from the molecular to the mesoscale. Thus, addressing specific battery issues such as functional capacity requires a comprehensive perspective initiating with atomic level concepts. For example, the electroactive materials which contribute to the functional capacity in a battery comprise approximately 30% or less of the total device mass. Thus, the design and implementation of multifunctional materials can conceptually reduce or eliminate the contribution of passive materials to the size and mass of the final system. Material multi-functionality can be achieved through appropriate material design on the atomic level resulting in bimetallic electroactive materials where one metal cation forms mesoscale conductive networks upon discharge while the other metal cation can contribute to atomic level structure and net functional secondary capacity, a device level issue. Specifically, this Account provides insight into the multi-mechanism electrochemical redox processes of bimetallic cathode materials based on transition metal oxides (MM'O) or phosphorous oxides (MM'PO) where M = Ag and M' = V or Fe. One discharge process can be described as reduction-displacement where Ag⁺ is reduced to Ag⁰ and displaced from the parent structure. This reduction-displacement reaction in silver-containing bimetallic electrodes allows for the *in-situ* formation of a conductive network, enhancing the

electrochemical performance of the electrode and reducing or eliminating the need for conductive additives. A second discharge process occurs through the reduction of the second transition metal, V or Fe, where the oxidation state of the metal center is reduced and lithium cations are inserted into the structure. As both metal centers contribute to the functional capacity, determining the kinetically and thermodynamically preferred reduction processes at various states of discharge is critical to elucidating the mechanism. Specific advanced *in-situ* and *ex-situ* characterization techniques are conducive to gaining insight regarding the electrochemical behavior of these multifunctional materials over multiple length scales. At the material level, optical microscopy, scanning electron microscopy, and local conductivity measurement via a nanoprobe can track the discharge mechanism of an isolated single particle. At the mesoscale electrode level, *in-situ* data from synchrotron based energy dispersive X-ray diffraction (EDXRD) within fully intact steel batteries can be used to spatially map the distribution of silver metal generated through reduction displacement as a function of discharge depth and discharge rate. As illustrated here, appropriate design of materials with multiple electrochemically active metal centers and properties tuned through strategically conceptualized materials synthesis may provide a path toward the next generation of high energy content electroactive materials and systems. Full understanding of the multiple electrochemical mechanisms can be achieved only by utilizing advanced characterization tools over multiple length scales.

1.0 Introduction

In a conventional electrode design, the electroactive material is combined with a conductive additive where each material plays a distinct role. Through appropriate material design, multi-functionality can be achieved for electroactive bimetallic materials where each metal center contributes to electrode function in a distinctive manner. Specifically, bimetallic oxide (MM'O) or phosphate (MM'PO) materials can undergo reactions during discharge (lithiation), where one metal ion (M^{m+}) is reduced to the metallic state (M^0) and repositioned externally to the original crystal through a reduction-displacement process, while the other metal ion (M'^{n+}) is partially reduced and structurally contributes to the crystal framework.¹⁻¹⁰

When M^{m+} (Ag^+ or Cu^{2+}) is part of the structure, Ag^0 or Cu^0 may form, which may positively impact the battery's relevant electrochemistry due to the high electrical conductivities of Ag^0 and Cu^0 .^{11,12} Copper and silver, while both coinage metals, behave quite differently in these bimetallic systems. While Cu^{2+} can be reduced to Cu^0 , it is often reintegrated into the layered structure upon charge¹³⁻¹⁵ and may be so finely divided that there is no notable increase in conductivity. In contrast, the reduction-displacement in silver vanadium phosphorous oxides, such as $Ag_2VO_2PO_4$, has been demonstrated to generate an *in-situ* conductive percolation Ag^0 network with an accompanying increase in conductivity of 15,000-fold.¹⁶ The second metal center, M'^{n+} (V, Fe, or W), may demonstrate multiple discharge/charge cycles in which both the oxidized and the reduced metal centers contribute structurally to the respective electrode materials.^{13,17-19} Notably, silver does not re-enter the parent structure upon charge,¹⁹ thus the conductivity benefit of the Ag^0 framework can be sustained upon full discharge and subsequent charge. Conceptually, on a volumetric energy density basis,

the replacement of carbon by silver could provide a five fold reduction in the volume of the conductive component. Consequently, bimetallic materials can be designed to contribute in two distinct ways to battery electrochemistry and display unique, reproducible, and desirable properties which are tunable through synthetic manipulation.

This Account provides a focused discussion of the multi-functional electrochemistry of bimetallic cathode materials (transition metal oxides ($MM'O$) or phosphorous oxides ($MM'PO$) where $M = Ag$ and $M' = V, Fe$). Mechanistically, a reduction-displacement takes place where Ag^+ is reduced to Ag^0 and displaced from the parent structure. A second type of discharge process occurs through the reduction of the second transition metal, V or Fe, accompanied by lithium cation insertion into the structure. Characterization of the multi-mechanism discharge process is highlighted where the use of advanced characterization techniques over multiple length scales yields insight regarding the electrochemical behavior of these multifunctional materials.

2.0 Bimetallic Silver Vanadium Oxide ($Ag_2V_4O_{11}$) and Silver Vanadium Phosphorous Oxides ($Ag_2VO_2PO_4$, $Ag_{0.48}VOPO_4$, $Ag_2VP_2O_8$)

The lithium/silver vanadium oxide ($Li/Ag_2V_4O_{11}$) system has been successfully commercialized and is commonly used as the power source for implantable cardiac defibrillators (ICDs).^{20,21} For lithium primary batteries, non-lithiated materials such as $Ag_2V_4O_{11}$ can be implemented as cathodes. The selection of silver vanadium oxide for the application was motivated by its ability to create a conductive network within the cathode due to reduction of Ag^+ , therefore, providing the high pulse power demanded by the ICD.^{22,23, 24} Analysis of $Li_xAg_2V_4O_{11}$ discharge products (x = moles of Li^+ inserted) indicated that the reduction of Ag^+ to Ag^0 occurs from $0 < x < 2.4$ with partial reduction of vanadium (V) occurring simultaneously.^{25,26,27} The reduction of the silver cation contributes ~30% of the capacity and significantly improves the cathode conductivity.²⁵ In the region $2.4 < x < 3.8$, the discharge process is dominated by reduction of V^{5+} to V^{4+} . Upon continued reduction to $x > 3.8$, reduction of V^{4+} to V^{3+} is observed.

The investigation of silver vanadium phosphorous oxide materials such as $Ag_2VO_2PO_4$, $Ag_{0.48}VOPO_4$, and $Ag_2VP_2O_8$ was motivated by increased structural stability provided by the inclusion of the phosphate structure. The stability was demonstrated by decreased solubility, providing the opportunity for increased battery lifetime.²⁸⁻³¹

Structure. $Ag_2V_4O_{11}$, $Ag_2VO_2PO_4$, $Ag_{0.48}VOPO_4$, and $Ag_2VP_2O_8$ are layered bimetallic materials containing silver (Ag^+) and vanadium ($V^{4+/5+}$) in which silver cations reside between vanadium oxide or phosphate layers.¹⁰ The structures are illustrated in **Figure 1**^{11,32-34} where the core structural unit consists of distorted VO_6 octahedra which link through edges or corners to other VO_6 octahedra or PO_4 tetrahedra to form infinite chains or layers. The silver ions are stabilized in an octahedral coordination environment, typically surrounded by oxygen from VO_6 while water molecules also co-occupy the interlayers in $Ag_{0.48}VOPO_4$. The layered motif of these materials permits

mobility of silver cations within the interlayer space, contributing to the high capacity which can reach up to 450 mAh/g (**Table 1**) and high pulse capability.^{10,19,35-41}

Electrochemical Reduction. Despite the structural similarities of silver vanadium oxide and silver vanadium phosphate materials, the electrochemical behavior of each material varies. Discharge profiles of the materials are shown in **Figure 2** and demonstrate single or multiple plateaus.^{37,39,42,43} $\text{Ag}_2\text{V}_4\text{O}_{11}$ displays two distinct plateaus at 2.7 V and 2.5 V, while $\text{Ag}_2\text{VO}_2\text{PO}_4$ demonstrates one long plateau at 2.7 V. The vanadium oxidation state in $\text{Ag}_{0.48}\text{VOPO}_4$ is mixed valent ($\text{V}^{+5}/\text{V}^{4+}$), while the vanadium center in $\text{Ag}_2\text{VP}_2\text{O}_8$ is V^{4+} . Synthetic approaches^{44,45} and the discharge mechanisms of the materials have been studied in detail using spectroscopic,^{18,46} magnetic susceptibility,⁴⁷ conductivity,^{16,47} and diffraction techniques.^{37,48-50} As there are two metal centers, the reduction mechanisms relate to the oxidation state of vanadium and silver content of the material and the overall discharge mechanisms are summarized in **Table 1**. Notably, the discharge rate can have profound effects on the reaction progression and impact the relative ratio of Ag^+ and $\text{V}^{5+}/\text{V}^{4+}/\text{V}^{3+}$ reduction.^{35,50}

Particle Level Characterization. Upon reduction of the bimetallic vanadium-based materials, nano-sized clusters of metallic silver form on the surfaces of particles which can be detected by scanning electron microscopy (SEM) (**Figure 3**).¹⁶ A limited number of quantitative electrochemical studies of individual particles have been reported where the lithiation of individual particles of pure active material was conducted. These studies provide the ability to interrogate the intrinsic properties of the active material directly without complications of other components commonly present in electrodes such as binders and conductive additives. Optical visualization of the reduction-displacement process upon discharge of a single particle of $\text{Ag}_2\text{VO}_2\text{PO}_4$ was recently reported (**Figure 4a**).⁵¹ During discharge, a transparent orange $\text{Ag}_2\text{VO}_2\text{PO}_4$ crystal gradually turned black as the electrochemical reaction front moved along the c-direction of the crystal. The concomitant color change is related to the formation of silver nanoparticles on the surface of the crystal as well as the formation of a vanadium bronze-type material. Conductivity measurements of a partially discharged $\text{Ag}_2\text{VO}_2\text{PO}_4$ particle were executed by using a scanning transmission microscopy tip on orange (undischarged) and dark (discharged) regions (**Figure 4b**). The data revealed that the black (discharged) region of $\text{Ag}_2\text{VO}_2\text{PO}_4$ possesses 100,000 times lower resistance compared to the undischarged, orange region, consistent with bulk $\text{Ag}_2\text{VO}_2\text{PO}_4$ electrode data.¹⁶

Mesoscale Electrode Characterization: Pure Electroactive Material. X-ray diffraction (XRD) can be used to detect low quantities of crystalline Ag^0 , formed upon reduction displacement, since Ag^0 is a high Z element which displays intense diffraction peaks.³⁷ Electrodes comprised of pure $\text{Ag}_2\text{VO}_2\text{PO}_4$ were electrochemically reduced under a constant current C/200 rate, and the process was monitored via *ex-situ* XRD.¹⁶ As discharge progressed, the parent $\text{Ag}_2\text{VO}_2\text{PO}_4$ peak intensity decreased monotonically while the Ag^0 peak intensity increased up to $x = 2.4$ molar electron equivalents of reduction in $\text{Li}_x\text{Ag}_{2-x}\text{VO}_2\text{PO}_4$. If the mechanism were to proceed stepwise with complete reduction of $\text{Ag}^+ \rightarrow \text{Ag}^0$, followed by reduction of V^{5+} , then the Ag^0 peak intensity would be expected to reach its maximum at $x = 2.0$. Therefore, these XRD data

suggested reduction of Ag^+ and V^{5+} can occur in parallel, as confirmed by magnetic susceptibility of vanadium⁴⁷ and X-ray absorption spectroscopy¹⁸ studies. AC impedance indicated an increase in conductivity of >15,000 times as the cell was discharged from zero to 0.08 molar electron equivalents or 2% of the cell theoretical capacity, demonstrating the fundamental phenomenon that structural incorporation of a metal ion, reduced to metallic particles on initiation of reduction, can lead to a significant conductivity increase in an electrode of pure material which is free of conductive additives.

Electrochemical cells with X-ray transparent windows are important *in-situ* characterization tools, especially for lithium batteries; however, they do not fully replicate conditions within fully functioning cells. Energy dispersive X-ray diffraction (EDXRD) can penetrate engineered bulk materials permitting measurements through the stainless steel can of intact, operational coin cells and has achieved adequate spatial resolution to detect the *in-situ* formation of Ag^0 during reduction displacement of silver in $\text{Ag}_2\text{VO}_2\text{PO}_4$ and $\text{Ag}_2\text{VP}_2\text{O}_8$ cathodes.^{37,48-50} In particular, EDXRD provides spatially resolved information critical to mechanistic interpretation of the Ag^+ reduction-displacement reaction within the physical confines of battery electrodes and gives insight into electronic versus ionic limitations of the discharge process as well as rate dependent behavior.⁵⁰

In 2013, the first *in-situ* EDXRD analysis of an intact coin-sized lithium anode cell was performed for a pelletized $\text{Ag}_2\text{VO}_2\text{PO}_4$ cathode.³⁷ A representative experimental configuration of EDXRD studies is shown in **Figure 5a**. In a partially discharged cell, Ag^0 was observed on the side of the cathode nearest to the Li-anode while $\text{Ag}_2\text{VO}_2\text{PO}_4$ was dominant on the side of the cathode facing the stainless steel cell, illustrating a clear reaction front within the cathode. A fully discharged cell showed the presence of Ag^0 throughout the cathode.³⁷ The *in-situ* EDXRD data agrees with previous *ex-situ* XRD data which established that the multi-mechanism processes during discharge of $\text{Ag}_2\text{VO}_2\text{PO}_4$ (i.e. $\text{Ag}^+ \rightarrow \text{Ag}^0$ and vanadium reduction) occur in parallel.

In addition to locational dependence as a function of discharge depth, lithiation and reduction-displacement mechanisms can be rate-dependent in pure $\text{Ag}_2\text{VP}_2\text{O}_8$ cathodes. EDXRD analysis of lithium cells containing $\text{Ag}_2\text{VP}_2\text{O}_8$ cathodes was conducted on cells discharged at slower (C/1440) and faster (C/168) rates (**Figure 5b/5c**).⁵⁰ Evidence of Ag^0 was observed on the surface of the lithium anode and attributed to ion-exchange (Li^+ for Ag^+) of the cathode material (Ag^+) with the electrolyte (Li^+) while Ag^0 observed near the stainless steel can was associated with reduction displacement.^{28,51} In $\text{Ag}_2\text{VP}_2\text{O}_8$ cathodes, the quantity, distribution, and crystallite size of Ag^0 show a strong dependence on discharge rate. $\text{Ag}_2\text{VP}_2\text{O}_8$ cathodes subjected to high discharge rates produced highly crystalline Ag^0 (~500 nm crystallite size) and localized formation of Ag^0 particles (indicative of uneven discharge), whereas slower discharge rates afforded more evenly distributed, nanocrystalline Ag^0 (~5 nm crystallite size), suggesting homogeneous lithiation (**Figure 5b/5c**).⁵⁰ Cells discharged at faster rates demonstrated approximately 3X higher charge transfer resistance compared to cells discharged at slower rates. Slower discharge rates produced almost 2X as much silver as the Li/ $\text{Ag}_2\text{VP}_2\text{O}_8$ cells discharged at faster rates, up to 1 electron equivalent,

suggesting that reduction of silver is more prominent than reduction of V^{4+} species at slow discharge rates. Notably, the uniform dispersion of nanocrystalline Ag^0 , observed under the slower discharge rate, reduces the resulting impedance.

Mesoscale Electrode Characterization: The Role of Conductive Additives.

Electronic conductivity is essential for full utilization of cathode materials and increases the electrode's ability to achieve high delivered capacities, ideally approaching theoretical values. Consequently, conductive additives, including conductive polymers and carbonaceous additives, are widely utilized during cathode preparation. Traditional conductive additives are electrochemically inactive and decrease the gravimetric and/or volumetric capacity of the composite cathode. In comparison, the formation of Ag^0 metal nanoparticles in $Ag_2V_4O_{11}$ and $Ag_2VO_2PO_4$ substantially contributes to capacity. The volume percentage of Ag^0 required to achieve a percolation threshold has been estimated to be $\sim 0.3\%$ of the total volume of $Ag_2VP_2O_8$.⁴⁸ Thus, at $<1\%$ electrochemical reduction for $Ag_2VP_2O_8$, sufficient silver can be generated to reach the percolation threshold and form a conductive cathode matrix. These results indicate that the silver content in bimetallic $Ag_2V_4O_{11}$ and $Ag_2VO_2PO_4$ materials is more than sufficient to achieve a conductive network.

The effect of conductive additives, in relation to Ag^0 displacement, in $Ag_2VP_2O_8$ cathodes was recently investigated.⁴⁹ A combination of *in-situ* and *ex-situ* characterization techniques (EDXRD, X-ray absorption (XAS), and AC impedance) was utilized to determine the role of a conductive carbon additive at various depths of discharge in Li/ $Ag_2VP_2O_8$ cells. The carbon additive enabled the formation of Ag^0 with uniform distribution upon reduction largely independent of discharge rate. EDXRD spectra of discharged cathodes showed larger full width at half-maximum (FWHM) values and lower intensities of Ag^0 peaks in cathodes discharged at faster (C/168) rates, consistent with a smaller crystallite size (11 nm), while an Ag^0 crystallite size of 40 nm was observed in cells discharged at slower (C/1440) rates. For cells containing carbon in the cathode, the impedance responses were dependent on the size of Ag^0 nanoparticles, rather than the quantity of silver, and lower resistivity was observed for cells discharged at fast rates with smaller Ag^0 nanoparticles which indicates establishment of a superior conductive network. The transition of $Ag^+ \rightarrow Ag^0$ was also monitored by *ex-situ* XAS and linear combination fitting determined that silver metal content was equivalent for both fast and slow rates and increases with depth of discharge. The data affirm that the inclusion of conductive carbon in the cathode enables more uniform discharge and distribution of Ag^0 metal. Notably, even in the presence of a carbon additive in the cathode, the impedance of the cells decreases significantly on initiation of discharge indicating the additional benefit from the formation of silver metal. Thus, a pre-existing percolation network may be a necessary, but not a sufficient condition, for full utilization of the electroactive material.⁵²

3.0 Bimetallic Silver Iron Oxide ($AgFeO_2$)

Structure. Silver ferrite ($AgFeO_2$) is a bimetallic oxide containing alternating layers of edge-shared FeO_6 octahedra (Fe^{3+} oxidation state) with layers of close-packed Ag^+ cations between. The Ag^+ transition metal cations are linearly coordinated between two oxygen molecules in the parallel iron oxide layers. Two major polytypes of this

delafossite compound exist upon crystallization, either a rhombohedral (3R) or hexagonal (2H) geometry is possible based on the manner in which alternating iron oxide layers stack (**Figure 6a/6b**).^{53,54} The layers of the 3R polytype stack in an AaBbCcAaBbCc sequence while the 2H polytype layers stack as AaBbAaBb. Synthesis of silver ferrite via a co-precipitation reaction has been accomplished.⁵⁵ Further, silver ferrite/maghemite composites with Ag/Fe ratios ranging from 0.2-1.0 have also been prepared via direct *in-situ* formation through co-precipitation.⁵⁶ The nanocrystalline silver ferrite (10-18 nm) as a mixture of 2H and 3R-AgFeO₂ phases was identified via XRD and the poorly crystalline iron oxide phase (maghemite, γ -Fe₂O₃) was indicated by Raman spectroscopy (**Figure 6c**).

Electrochemical Reduction. Silver ferrite has recently been studied as a cathode material for lithium based batteries and displays multi-mechanism behavior.^{55,56} Examination of the discharge capacity revealed a decrease in delivered capacity between cycles 1 and 2 where the capacity difference was directly proportional to the Ag⁺ content (**Figure 6d**).⁵⁶ which can be rationalized as the reduction displacement of Ag⁺ to Ag⁰. XRD of the cathode after discharge to 1 electron demonstrates decreased peak intensities of AgFeO₂ (i.e. amorphization of crystal structure) but no observable Ag⁰ peaks. The absence of Ag⁰ in the XRD suggests that the displaced Ag⁰ is nanocrystalline and cannot be detected by diffraction. AC impedance measurements demonstrate nearly a 6,000-fold decrease in resistivity of the silver ferrite/maghemite system upon discharge to 2 electron equivalents which can be correlated to the formation of Ag⁰.⁵⁵ Calculations show that a discharge of 0.05 electron equivalents (2.5% discharge) or greater would afford sufficient Ag⁰ content in AgFeO₂ and silver ferrite/maghemite materials necessary to achieve a conductive network. The silver ferrite/maghemite composite material with the lowest silver content, 0.2 Ag/Fe, displayed a capacity of 130 mAh/g with negligible fade over 50 cycles, suggesting that the redox process the Fe center is largely electrochemically reversible, while that at the Ag center is not.⁵⁶ Such results demonstrate the advantage of incorporating bimetallic materials in the direct preparation of nanocomposites for use as cathodes in secondary batteries. Notably, direct preparation of the nanocomposite gave improved electrochemical performance relative to mechanically mixing two separate oxide materials, likely due to the physiochemical differences between a mechanical mixture and a directly prepared bimetallic multifunctional material.

4.0 Conclusion

The presence of two distinct electrochemically active metal cations in bimetallic cathode materials in lithium batteries can provide complementary battery electrochemistry, such as high current capabilities with minimal conductive additives. Further, by combining two diverse metals within one material, the effects are tunable via synthesis, given careful control of the ratios of the metals within the phase. This Account describes several layered structures with crystalline motifs that provide enhanced mobility of Li⁺ and Ag⁺ ions. The multi-mechanism discharge process of silver-containing bimetallic cathodes enables the reduction displacement of Ag⁰, which can initiate the *in-situ* formation of a conductive percolation network of metallic nanoparticles, and insertion/de-insertion of lithium ions within a metal oxide structure.

Single-particle electrochemistry has provided considerable insight into the steps associated with the electrochemical behavior of multifunctional bimetallic materials. Spatial characterization of the discharge processes within a cathode has been demonstrated using synchrotron based energy dispersive X-ray diffraction (EDXRD) of fully intact steel battery cells. Multifunctional electrode materials can provide a path toward increased energy density. Investigation over multiple length scales is necessary to effectively characterize the electrochemical processes.

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Biographical Information

Jessica L. Durham obtained a BS and MS in chemistry from Illinois State University. She is currently a senior PhD candidate in the Department of Chemistry at Stony Brook University conducting research under the supervision of Dr. Esther S. Takeuchi, Dr. Kenneth J. Takeuchi, and Dr. Amy C. Marschilok. Her research includes the electrochemical investigation of nanocrystalline bimetallic iron and manganese oxides (prepared via aqueous, low-temperature approaches which are eco-friendly and economically feasible) as viable cathode materials for lithium batteries.

Altug S. Poyraz is a post doctoral research associate at Brookhaven National Laboratory under the supervision of Prof. Esther S. Takeuchi. Dr. Poyraz received his BS and MS from Bilkent University Chemistry department and a PhD in chemistry from the University of Connecticut. His research focuses on the synthesis and characterization of transition metal oxide based cathode materials for rechargeable lithium batteries.

Esther S. Takeuchi is a SUNY Distinguished Professor in the Departments of Chemistry and Materials Science and Engineering at Stony Brook University and holds a joint appointment at Brookhaven National Laboratory. She received a BA in chemistry and history from the University of Pennsylvania and a PhD in chemistry from Ohio State University. Prior to her academic career, she conducted battery research in industry, particularly for implantable applications. She is a member of National Academy of Engineering, National Inventors Hall of Fame, and National Academy of Innovation and has received the National Medal of Technology and Innovation. Her research focus is on understanding governing mechanisms related to energy storage.

Amy C. Marschilok is a Research Professor in the Departments of Materials Science and Engineering and Chemistry at Stony Brook University. She received her BA and PhD in Chemistry from the University at Buffalo. She was previously employed at Greatbatch Inc., where she was recognized as a Visionary of the Year. She received the Leadership Award, Professional Service Category, from the Western New York YWCA. She was also recognized as a Woman of Distinction by the Girl Scouts of Western New York. Her research involves synthesis, advanced characterization, and electrochemical study of novel materials and systems for energy storage.

Kenneth J. Takeuchi is a SUNY Distinguished Teaching Professor in the Department of Chemistry at Stony Brook University. He holds a BS in chemistry from the University of Cincinnati and a PhD in chemistry from The Ohio State University and is a Fellow of the American Chemical Society and a Fellow of the American Association for the Advancement of Science. Professor Takeuchi has received over 20 regional and national awards for excellence in teaching and mentoring. His research involves the synthesis and utility of inorganic materials towards energy storage with a recent focus on synthetic development for crystallite size control.

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Figure 1. Crystal structures of silver vanadium oxide and silver vanadium phosphorous oxide layered materials: (a) $\text{Ag}_2\text{V}_4\text{O}_{11}$,¹¹ (b) $\text{Ag}_2\text{VO}_2\text{PO}_4$,³² (c) $\text{Ag}_{0.48}\text{VOPO}_4$,³³ (d) $\text{Ag}_2\text{VP}_2\text{O}_8$.³⁴

Figure 2. Galvanostatic discharge profiles of (a) $\text{Li}/\text{Ag}_2\text{V}_4\text{O}_{11}$,³⁹ (b) $\text{Li}/\text{Ag}_2\text{VO}_2\text{PO}_4$,⁴³ (c) $\text{Li}/\text{Ag}_{0.48}\text{VOPO}_4$,⁴² and (d) $\text{Li}/\text{Ag}_2\text{VP}_2\text{O}_8$ ³⁷ plotted with respect to electron equivalents. Graphs a, c, and d adapted with permission from Ref. 39, 42, and 37, copyright 2016 Elsevier. Graph (b) adapted and reproduced from Ref. 43 by permission of The Royal Society of Chemistry.

Figure 3. Scanning electron microscopy (SEM) images of (a) pristine $\text{Ag}_2\text{VO}_2\text{PO}_4$ and (b) $\text{Ag}_2\text{VO}_2\text{PO}_4$ discharged (lithiated) to 0.8 molar electron equivalents with Ag^0 nanoparticles discernible on the surface of the particle.¹⁶ Images adapted with permission from Ref. 16. Copyright 2016 American Chemical Society.

Table 1. Discharge mechanisms and theoretical capacities of silver vanadium oxide and silver vanadium phosphorous oxide materials.

Material	Lithiation Mechanism		Theoretical Capacity (mAh/g)
Ag₂V^V₄O₁₁ 10,39-41	$\text{Ag}_2\text{V}_4^{\text{V}}\text{O}_{11} + x \text{Li}^+ + x \text{e}^- \rightarrow \text{Li}_x\text{Ag}_2\text{V}_x^{\text{IV}}\text{V}_{4-x}^{\text{V}}\text{O}_{11}$ $\text{Li}_{0.7}\text{Ag}_2\text{V}_x^{\text{IV}}\text{V}_{4-x}^{\text{V}}\text{O}_{11} + y \text{Li}^+ + y \text{e}^- \rightarrow \text{Li}_{0.7+y}\text{Ag}_{2-m}\text{V}_{x+n}^{\text{IV}}\text{V}_{4-x-n}^{\text{V}}\text{O}_{11} + m \text{Ag}^0$ $\text{Li}_{5.5}\text{Ag}_{2-m}\text{V}_{x+n}^{\text{IV}}\text{V}_{4-x-n}^{\text{V}}\text{O}_{11} + z \text{Li}^+ + z \text{e}^- \rightarrow \text{Li}_{5.5+z}\text{Ag}_{2-m}\text{V}_{\varepsilon}^{\text{III}}\text{V}_{x+n+z}^{\text{IV}}\text{O}_{11} \quad (m \sim 2)$	$x \leq 0.7$ $0.7 \leq y \leq 5.5$ $(y = m + n)$ $z \leq 4.5$ $\varepsilon = \text{trace}$	450 (10 e ⁻ equiv.)
Ag₂VO₂PO₄ 16,18,37,47	$\text{Ag}_2\text{V}^{\text{V}}\text{O}_2\text{PO}_4 + x \text{Li}^+ + x \text{e}^- \rightarrow \text{Li}_x\text{Ag}_{2-m}\text{V}_n^{\text{IV}}\text{V}_{1-n}^{\text{V}}\text{O}_2\text{PO}_4 + m \text{Ag}^0 \quad (m \gg n)$ $\text{Li}_2\text{Ag}_{2-m}\text{V}_n^{\text{IV}}\text{V}_{1-n}^{\text{V}}\text{O}_2\text{PO}_4 + y \text{Li}^+ + y \text{e}^- \rightarrow \text{Li}_{2+y}\text{V}_m^{\text{III}}\text{V}_n^{\text{IV}}\text{V}_{1-2-m-n}^{\text{V}}\text{O}_2\text{PO}_4$	$x \leq 2$ $(x = m + n)$ $y \leq 2$ $(y = m + n)$ $\varepsilon = \text{trace}$	270 (4 e ⁻ equiv.)
Ag_{0.48}VOPO₄ 19,42	$\text{Ag}_{0.48}\text{V}^{\text{IV}}_{0.48}\text{V}^{\text{V}}_{0.52}\text{OPO}_4 + x \text{Li}^+ + x \text{e}^- \rightarrow \text{Li}_x\text{Ag}_{0.48}\text{V}^{\text{IV}}_{0.48+x}\text{V}^{\text{V}}_{0.52-x}\text{OPO}_4$ $\text{Li}_{0.52}\text{Ag}_{0.48}\text{V}^{\text{IV}}\text{OPO}_4 + y \text{Li}^+ + y \text{e}^- \rightarrow \text{Li}_{0.52+y}\text{Ag}_{0.48-y}\text{V}^{\text{IV}}\text{OPO}_4 + y \text{Ag}^0$ $\text{LiV}^{\text{IV}}\text{OPO}_4 + z \text{Li}^+ + z \text{e}^- \rightarrow \text{Li}_{1+z}\text{V}_z^{\text{III}}\text{V}_{1-z}^{\text{IV}}\text{OPO}_4$	$x \leq 0.52$ $y \leq 0.48$ $z \leq 0.26$	310 (2.48 e ⁻ equiv.)
Ag₂VP₂O₈ 37,48,51	$\text{Ag}_2\text{V}^{\text{IV}}\text{P}_2\text{O}_8 + x \text{Li}^+ + x \text{e}^- \rightarrow \text{Li}_x\text{Ag}_{2-m}\text{V}_n^{\text{III}}\text{V}_{1-n}^{\text{IV}}\text{P}_2\text{O}_8 + m \text{Ag}^0$ $\text{Li}_2\text{Ag}_{2-m}\text{V}_n^{\text{III}}\text{V}_{1-n}^{\text{IV}}\text{P}_2\text{O}_8 + y \text{Li}^+ + y \text{e}^- \rightarrow \text{Li}_{2+y}\text{V}_n^{\text{III}}\text{V}_{1-n}^{\text{IV}}\text{P}_2\text{O}_8 + y \text{Ag}^0$	$x \leq 2$ $(x = m + n)$ $2 \leq y \leq 3$	176 (3 e ⁻ equiv.)

a)

b)

Figure 4. (a) Constant current discharge of an individual $\text{Ag}_2\text{VO}_2\text{PO}_4$ particle. Blue diamonds in the voltage profile correspond to the optical images (shown at right) taken during discharge. (b) Optical and SEM images of a partially discharged $\text{Ag}_2\text{VO}_2\text{PO}_4$ particle. Images (Y) and (Z) illustrate the placement of STM tips for resistance measurements of the orange and dark regions of the particle (X), respectively.⁵¹ Reproduced from Ref. 51 by permission of The Royal Society of Chemistry.

Figure 5. (a) Experimental configuration used for *in-situ* energy dispersive X-ray diffraction (EDXRD) measurements of Li/Ag₂VP₂O₈ coin cells. (b,c) Intensities of Ag⁰ and Ag₂VP₂O₈ and crystallite size of Ag⁰ displayed as a function of beam position along the z direction for cathodes discharged to 0.5 electron equivalents with discharge rates of: (b) C/168 (fast) and (c) C/1440 (slow). Separate locations were measured for fast and slow discharge rates, respectively.^{48,50} Image (a) reproduced from Ref. 48 with permission from the PCCP Owner Societies. Images (b) and (c) reproduced from Ref. 50 and reprinted with permission from AAAS.

Figure 6. Structures of silver ferrite: (a) 2H-AgFeO₂⁵³ and (b) 3R-AgFeO₂.⁵⁴ (c) X-ray diffraction (XRD) and Raman spectroscopy of silver ferrite composites as-prepared. (d) Plot demonstrating capacity loss from cycle 1 to cycle 2 as a function of electron count.⁵⁶ Graphs (c) and (d) adapted and reproduced from Ref. 56 by permission of The Royal Society of Chemistry.