Dynamic Study of (De)sodiation in **alpha**-MnO₂ nanowires

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Abstract:

In this report, the electrochemical sodiation and desodiation in single crystalline α -MnO₂ nanowires are studied dynamically at both single particle level using *in situ* transmission electron microscopy (TEM) and bulk level using *in situ* synchrotron X-ray. The TEM results suggest that the first sodiation process starts with tunnel-based Na⁺ intercalation, experiences the formation of Na_{0.5}MnO₂ as a result of tunnel degradation, and ends with the Mn₂O₃ phase. The inserted Na⁺ can be partially extracted out of the sodiated products, and the following cycles are dominated by the reversible conversion reaction between Na_{0.5}MnO₂ and Mn₂O₃. The Mn valence evolution inside a cycling coin using α -MnO₂ nanowire electrode also exhibits partially reversible characteristic, agreeing well with the *in situ* TEM analysis. The sodiation is compared with lithiation in the same α -MnO₂ nanowires. Both Na⁺ and Li⁺ interact with the tunneled structure *via* a similar tunnel-driven intercalation mechanism before Mn⁴⁺ is reduced to Mn^{3.5+}. For the following deep insertion, the tunnels survive up to LiMnO₂ (Mn³⁺) during lithiation, while the sodiation proceeds *via* a different mechanism that involves obvious phase transition and fast tunnel degradation after Mn's valence is below 3.5+. The difference in charge carrier insertion mechanisms can be ascribed to the strong interaction between the tunnel frame and inserted Na⁺ possessing a larger ionic size than inserted Li⁺.

Key Words: *in situ* TEM; tunnel; α -MnO₂; sodium ion battery; Mn valence

1. Introduction:

Lithium ion batteries (LIB) have led the market of rechargeable energy storage devices for decades as a high-energy power source.¹ However, due to the limited storage of Li source in the Earth's crust and the wide-scale implementation of renewable energy in the fields of electric vehicles and portable devices, the world is now driven to explore new charge carriers as Li alternatives.² Compared with Li^+ , Na^+ possesses the same amount of charge while its resources are much richer in the world, making sodium ion batteries (NaIB) the ideal alternative to LIB.³ A substantial amount of research has been devoted to the development of electrode materials for NaIB, including nanostructured manganese oxides.^{3,4,5}

Manganese oxides are well known for the various polymorphs possessing different open structures to facilitate the initial Na^+ insertion. Materials of this family include orthorhombic $\text{Na}_{0.44}\text{MnO}_2$,^{6,7} $\text{Na}_{0.66}\text{MnO}_2$,⁸ $\beta\text{-NaMnO}_2$,⁹ and $\alpha\text{-(}\beta\text{-, } \lambda\text{-)}\text{MnO}_2$ ^{10,11,12,13}, whose initial discharge capacity can be as high as 350 mAh/g. However, these materials always suffer from poor cycling performance with their capacity decaying very fast to even below 100 mAh/g before reaching 100 cycles.^{8,11} Although it has been explained theoretically that the fast capacity decay is due to the relatively large size of Na^+ compared with Li^+ that strongly affects the host structure, no *in situ* work has been performed to identify the character of such interactions. Besides, the dynamic response of nanostructured manganese oxides during repetitive (de)sodiation is currently not reported yet, leading to the lack of knowledge on the underlying electrochemical mechanisms.

In this report, α -MnO₂ nanowires featuring one dimensional tunneled structure (Supporting Information Figure S1) are studied by monitoring the morphology and phase evolution during electrochemical (de)sodiation using *in situ* transmission electron microscopy (TEM). It is found that the tunneled structure of α -MnO₂ maintains stable until Mn⁴⁺ is reduced to Mn^{3.5+}, and the following deep sodiation lead to formation of Mn₂O₃ with polycrystalline Na₂O. An intermediate phase Na_{0.5}MnO₂ is discovered during the first sodiation. This phase dominates the rest of (de)sodiation cycles through a reversible conversion reaction with Mn₂O₃ polycrystals. The Mn valence evolution during (dis)charge of α -MnO₂ at the coin cell level is also studied by *in situ* X-ray Absorption Spectroscopy (XAS) measurement, the result of which agrees well with the TEM observation. The sodiation of α -MnO₂ nanowires is further compared with our previous lithiation study of the same type of nanowires to understand the different electrochemical mechanisms of the cation-tunnel interactions. The initial sodiation and lithiation proceed by the same tunnel-driven intercalation mechanism until Mn⁴⁺ is reduced to Mn^{3.5+}. For the following deep cation insertion, the tunnels can survive up to LiMnO₂ (Mn³⁺) during lithiation, while the sodiation process results in fast tunnel degradation and intermediate phase formation around Mn^{3.5+}, which is ascribed to the much stronger effect from inserted Na⁺ than Li⁺ on the host structure.

2. Materials and Methods

2.1 Material Synthesis.

The nanowires are synthesized by a hydrothermal method using KMnO_4 and MnSO_4 as the raw materials.¹⁴ During the formation of the tunneled structure in solution, K^+ will be automatically trapped inside the tunnels.

2.2 Open cell design in TEM.

The open cell is built using the *in situ* STM TEM holder equipped with two dangling gold tips being connected to the outside circuit. The nanowires are glued to one Au tip by conductive epoxy, and the metallic sodium is attached to the other Au tip by scratching the tip across the surface of a sodium foil in glovebox. During the holder transfer into the TEM chamber, sodium metal is partially oxidized to Na_2O , which functions as the solid electrolyte in the open cell design. The piezo-controlled movement is operated at single nanowire level to make it connected to the $\text{Na}/\text{Na}_2\text{O}$ on the other side, and an appropriate bias is then applied to initiate the sodiation process. The desodiation process is started by reversing the bias.

Both *ex situ* and *in situ* TEM are performed inside the JEOL JEM-ARM200CF equipped with a 200 KV cold field emission electron source. The elemental information is obtained using an Oxford X-max 100TLE windowless SDD X-ray detector.

2.3 Coin cell making.

The laminate contains $\alpha\text{-MnO}_2$ nanowires, PVDF and black P with the weight ratio of 8:1:1. The coin cell was assembled using $\alpha\text{-MnO}_2$ nanowires as the cathode, glass microfiber as the separator, NaPF_6 in EC/DEC as the electrolyte and metallic Na foil as

the anode. Punched coin cell cases and spacers with Kapton window were used to guarantee X-ray transmission at Mn K-edge.

2.4 *In situ* X-ray Absorption Spectroscopy.

The XAS measurement for the Mn K-edge was performed at the Advanced Photon Source (APS) on the bending-magnet beamline 9-BM-B with electron energy of 7 GeV and average current of 100 mA. The radiation was monochromatized by a Si (111) double-crystal monochromator. Harmonic rejection was accomplished with an Rh-coated mirror. All spectra were collected in transmission mode. For energy calibration, a Mn foil was measured simultaneously at the reference ionization chamber. The peak of the first derivative of Mn foil was adjusted to the tabulated value of 6539 eV. The coin cell was first discharged to 1 V and then charged back to 4 V at 0.1 C rate. X-ray absorption near edge spectra (XANES) data reduction and analysis were processed by Athena software.

3. Results and Discussions

3.1 Basic structure characterization.

The basic structural characterization of the nanowires from both the lateral and axial TEM imaging is given in Figure 1. Figures 1a and b show that the nanowire is monocrystalline with a uniform diameter of about 60 nm and a [001] growth direction. The [010] lateral HAADF imaging in Figure 1c illustrates the atomic structure of α -MnO₂. Referring to the model in Figure 1d, Mn (red dots) as the tunnel walls and K (green dots) in the tunnel center are clearly identified. The [001] axial TEM imaging in Figure 1e demonstrates a square-shaped cross section of the nanowire. The atomic structure of the

white framed area is given in Figure 1f, where the tunneled structure is directly captured with one 2×2 tunnel highlighted, surrounded by the Mn atoms (red dots) and occupied by one K⁺ atomic column (green dot). The accurate composition of the nanowire based on both the lateral and axial atomic imaging is thus determined to be K_{0.25}MnO₂. The inset of Figure 1f gives the atomic model, which agrees with the observation well.

3.2 *In situ* TEM of the sodiation and resulted phase evolution.

The sodiation of two α -MnO₂ nanowires is recorded in the Supporting Information Movie S1 and S2. It can be seen that the nanowires can be readily sodiated being evidenced by the obvious radial expansion. No apparent axial expansion is captured, indicating that the Na⁺ insertion is not an isotropic process. Despite the anisotropy, the host structure maintains stable as there is not any fracture or crack formation. To further explore the sodiation kinetics, the reaction front position is measured versus the sodiation time and the results are given in Supporting Information Figure S2. Both two curves generally follow the parabolic shape, which is the typical feature of a diffusion-controlled process described earlier by other *in situ* literatures^{15,16}. This indicates that the sodiation in α -MnO₂ nanowires is limited by Na⁺ diffusion instead of interface reaction.

Figure 2 shows the analysis of the phase transition from one partially sodiated nanowire. Four sections are defined based on their sodiated morphologies, i.e. the pristine section before sodiation (b), the slightly sodiated section (c), the heavily sodiated section (d) and the fully sodiated section (e). The Selected Area Electron Diffraction (SAED) patterns from these four sections are provided in Figure 2b-e, respectively. As shown in Figure 2b, the pristine nanowire is viewed along $[1\ 0\ \bar{1}]$ zone axis with the (0 2 0) lattice diffraction (yellow ring) directly seen with a spacing of 4.95 Å. For section (c) that is

slightly sodiated, the (0 2 0) spacing increases to 5.1 Å, which can be explained by the gradually enhanced Jahn-Teller distortion when more Mn^{4+} are reduced by the inserted Na^+ . Although the host lattice is severely distorted, the parent $\alpha\text{-MnO}_2$ phase is well maintained as evidenced by the remaining $[1\ 0\ \bar{1}]$ patterns, indicating that the 2×2 tunnels are still active for Na^+ insertion. However, several new ring-like diffractions (yellow arrows) are observed to coexist with the $\alpha\text{-MnO}_2$ patterns in Figure 2c and they are indexed to be $\text{Na}_{0.5}\text{MnO}_2$ (SG: Pnma). In the heavily sodiated section (d), the tunneled structure is totally degraded and the sole phase is indexed to be $\text{Na}_{0.5}\text{MnO}_2$. Upon the full sodiation, the metastable $\text{Na}_{0.5}\text{MnO}_2$ is finally converted to the polycrystalline Mn_2O_3 (white arrows) and Na_2O (green arrow) as confirmed in Figure 2e.

As such, the tunneled structure of $\alpha\text{-MnO}_2$ maintains its stability until 0.5 Na^+ are intercalated into the host with the subsequent formation of $\text{Na}_{0.5}\text{MnO}_2$ as an intermediate phase. The sodiation process can thus be written as a two-step based reaction:

The presence of K^+ is not considered in this part of discussion due to the complexity of different cations' interaction, which, however, is further addressed in the last discussion part.

3.3 *In situ* TEM of the sodiation/desodiation cycling.

The repetitive sodiation/desodiation of single nanowire is recorded in Supporting Information Movie S3. It shows that the nanowire expands during sodiation and reversibly contracts during desodiation, and no fracture or crack is observed up to five cycles, indicating the good reversibility of $\alpha\text{-MnO}_2$ nanostructures. The diameter of the

nanowire is measured versus the sodiation time, and the result is shown in Figure 3a. The first full sodiation results in about 50% radial expansion while the first desodiation only leads to 15% contraction. The expansion and contraction rates of the rest cycles are limited within 20%, indicating that the mechanism dominating the first sodiation of the nanowire must be different from the mechanism during the rest (de)sodiation cycles.

To clarify the different mechanisms, the phase evolution of the same nanowire is characterized for the first two cycles with the results illustrated in Figure 3b-g. The first full sodiation (Figure 3b-d) features the formation of an intermediate phase $\text{Na}_{0.5}\text{MnO}_2$ and the final conversion to Mn_2O_3 and Na_2O , which follows the similar two-step phase evolution as discussed in Figure 2. For the full desodiated phase, however, no crystalline $\alpha\text{-MnO}_2$ is detected, and the reformation of $\text{Na}_{0.5}\text{MnO}_2$ dominates the reaction. Some residual Na_2O polycrystals are detected, which is probably due to their poor electron conductivity that makes part of them difficult to decompose during desodiation. During the 2nd full sodiation, the $\text{Na}_{0.5}\text{MnO}_2$ is totally converted to Mn_2O_3 and Na_2O , while it appears again during the 2nd desodiation. So compared with the first sodiation process where $\alpha\text{-MnO}_2$ is sodiated to $\text{Na}_{0.5}\text{MnO}_2$ and finally converted to Mn_2O_3 and Na_2O , the following cycles are characterized by the reversible conversion reaction between $\text{Na}_{0.5}\text{MnO}_2$ and Mn_2O_3 . It is also notable in Figure 3g that in the fully desodiated state, Mn_2O_3 cannot be totally converted back to $\text{Na}_{0.5}\text{MnO}_2$, which can be explained by the gradual pulverization of Mn_2O_3 polycrystals during repetitive cycles that makes the electron path discontinuous inside Na_2O matrix. As such, it is expected that the following cycles should exhibit very quick capacity fading as more and more Na_2O accumulates in the electrode and thus gradually cuts off the electron conductive path. This capacity

fading mechanism can also explain the reported fast capacity decay of NaIBs using manganese oxides as the electrode.¹¹ It is apparent that certain methods should be utilized to improve the conductivity of Mn-based oxides for reversible Na⁺ storage, such as proper structure modification and surface coating of conductive materials.

3.4 Coin-cell level *in situ* XAS measurement for (de)sodiation.

To study the mechanism of the (de)sodiation process of MnO₂ nanowires in bulk scale, the cycling stability, the voltage profile and *in situ* XAS data were collected during the battery cycling where α -MnO₂ nanowires were utilized as cathode and Na metal as anode. The cycling results are provided in Figure S3. It shows that the Na-MnO₂ battery initially shows a discharge capacity of 300 mAh/g while the capacity drops quickly with the cycles. After 50 cycles, both discharge and charge capacities are below 50 mAh/g, indicating the poor cycling stability of MnO₂ electrode. The voltage profile during the first discharge/charge cycle is shown in Figure S4, where the discharge process exhibits one slope region (2.5 V – 1.3 V) and one plateau region (1.3 V – 1 V). The slope region should be related with the initial intercalation of Na⁺ into the tunneled structure and the plateau region should indicate the following conversion reaction to Mn₂O₃. It is notable that these two stages contribute almost equal discharge capacity, agreeing well with the *in situ* TEM results, where 0.5 Na⁺ first intercalate into tunneled MnO₂ (150 mAh/g in theory), and then extra 0.5 Na⁺ insertion results in the conversion reaction (150 mAh/g in theory). During the charge process, only about 130 mAh/g capacity is reversible, which also agrees with the partially reversible conversion from Mn₂O₃ to Na_{0.5}MnO₂ as confirmed by *in situ* TEM. Both the poor cycling stability and the large voltage hysteresis between discharge and charge can be ascribed to the poor reaction kinetics that is limited

by the gradual formation of electron-insulating Na₂O as well as the gradually isolated Mn-based redox centers.

In situ XANES spectra, which are used for identifying the oxidation state of Mn are shown in Figure 4a with the spectra of the standard Mn, MnO, Mn₂O₃ and MnO₂. The initial oxidation state of α -MnO₂ nanowires (red solid line) is slightly lower than 4⁺, compared with the standard MnO₂ (blue dashed line). During the discharge process, the oxidation state of Mn continuously decreased and was close to 3⁺ when fully discharged to 1V (green solid line). During the charge, the oxidation state of Mn increased obviously (from green to purple solid line) but it was not totally recovered to its pristine state even fully charged to 4 V. To quantitatively analyze the Mn oxidation state change, the liner combination fitting (LCF) of the *in situ* XAS spectra with standard Mn₂O₃ and MnO₂ was conducted. The LCF result with the battery discharge-charge profile is shown in Figure 4b. The initial oxidation state of the α -MnO₂ nanowires was $\sim 3.6^+$, which roughly matches the initial composition of the nanowires (K_{0.25}MnO₂). Then, it decreased to $\sim 3.1^+$ at the end of discharge. During charge, the oxidation state of Mn increased to $\sim 3.4^+$, which is probably in accordance with the state of charge observed in TEM when intermediate Na_{0.5}MnO₂ is the dominant phase. The fact that Mn cannot recover its oxidation state during charge to its initial state before discharge indicates that the first cycle is not totally reversible, which could be explained by the residual Na⁺ left in the α -MnO₂ nanowires that can not be totally extracted out. The *in situ* XAS results thus agree well with the *in situ* TEM observation in terms of the Mn valence evolution and the reversibility of the host structure.

3.5 Comparison between sodiation and lithiation in 2×2 tunnels.

It has been predicted that due to the size difference, Na^+ is inserted into the 2×2 tunnels of $\alpha\text{-MnO}_2$ *via* a distinct path compared with Li^+ .¹⁷ Specifically, many reports have pointed out that Li^+ prefers to diffuse along the Wyckoff 8h sites that are off-centered, while Na^+ thermodynamically occupies the near-centered position inside the 2×2 tunnels.^{17,18} Practically, since most hydrothermally synthesized $\alpha\text{-MnO}_2$ products inevitably have their 2×2 tunnels partially occupied by large cations (like K^+ in our case), the complicated reactions inside the host are more than just Li^+/Na^+ -tunnel interaction. It is thus expected here that $\alpha\text{-MnO}_2$ nanowire behaves distinctly during lithiation and sodiation in terms of tunnel stability, structure evolution, and phase transition.

To confirm this hypothesis, the *in situ* sodiation of the same $\alpha\text{-MnO}_2$ nanowires is compared with our previous *in situ* lithiation work¹⁸ with the results shown in Figure 5. Based on the EDS mappings of Mn, K and Na in Panel A and Panel B, it can be seen that both lithiation and sodiation can result in partial removal of K^+ from the inserted area while Mn atoms maintain stable. This should be ascribed to the repulsive forces exerted to K^+ from inserted Li^+ and Na^+ possessing the same positive charge. It is worth noting that Na^+ insertion has a stronger interaction with K^+ than Li^+ insertion does, resulting in more K^+ being removed from the inserted tunnels as evidenced by the measured K/Mn atomic ratio. This finding confirms the previous prediction that Na^+ , with a larger cation size (1.02 Å) than Li^+ (0.76 Å), diffuse through the host *via* a distinct path that is closer to the tunnel center.^{17,18} It is this centered path that results in stronger Na^+ and K^+ interaction because the latter atoms also occupy the tunnel center (Wyckoff 2a sites). The fact that K^+ are easier to be removed upon sodiation indicates that the tunneled structure

should be more vulnerable when it takes in Na^+ than Li^+ , which is further confirmed in Panel C of Figure 5.

It can be seen from Panel C that the phase evolutions during lithiation and sodiation are sharply different. The 2×2 tunneled structure of $\alpha\text{-MnO}_2$ is well maintained even one Li^+ are intercalated into the unit MnO_2 host.¹⁸ The tunneled structure becomes vulnerable when Na^+ ions diffuse in, and is totally replaced by a new phase even before 0.5 Na^+ are inserted in. Since it has been shown in Section 3.3 that the tunneled structure of $\alpha\text{-MnO}_2$ cannot be recovered once it is totally degraded, portion of the 1st discharge capacity contributed from the Na^+ intercalation is no longer counted in the following cycles. In the sense, this mechanism well explains the fast capacity fading of $\alpha\text{-MnO}_2$ as a NaIB electrode immediately after its 1st cycle, as well as the fact that Li/MnO_2 batteries generally exhibit higher cycleable capacity than Na/MnO_2 batteries.^{19,20,21}

It has been reported that large cations such as K^+ , Ba^{2+} and Ag^+ are required to stabilize the large 2×2 tunnel cavity of $\alpha\text{-MnO}_2$ and the 2×2 tunneled phase is more likely to form when the concentration of the large cations is high.^{22,23} Small cations such as H^+ , Li^+ and Na^+ would not efficiently support the tunnels without the presence of large cations.²⁴ Based on this, it is understandable that the tunneled structure is more vulnerable during sodiation than it is during lithiation, knowing that inserted Na^+ result in the removal of more K^+ from the tunnels than Li^+ do. It is also worth mentioning that in the current experimental conditions, it is difficult to quantitatively study the K^+ effect since K ions are hard to be dynamically tracked and imaged during Na^+ (Li^+) insertion, and the underlying interactions are more complicated than being discovered here. But it is reasonably to expect that future work, inspired by our current fundamental findings,

could clear this ambiguity, and the electrochemical performance of MnO_2 -based electrodes could be efficiently improved by proper structural and compositional modifications.

4. Conclusion

We reported for the first time the dynamic study of (de)sodiation mechanism in single α - MnO_2 nanowire combining both *in situ* TEM and *in situ* synchrotron XAS. During first sodiation cycle, the tunneled structure of α - MnO_2 can survive Na^+ insertion when Mn^{4+} is gradually reduced to $\text{Mn}^{3.5+}$. It is then followed by fast tunnel degradation with formation of an intermediate phase, $\text{Na}_{0.5}\text{MnO}_2$, and the final conversion to Mn_2O_3 and Na_2O . The 1st desodiation process and the following cycles are dominated by the partially reversible conversion reaction between $\text{Na}_{0.5}\text{MnO}_2$ and Mn_2O_3 . The comparison between lithiation and sodiation shows that the initial Na^+ and Li^+ insertion in α - MnO_2 proceed *via* the same tunnel-driven intercalation mechanism accompanied by tunnel expansion until Mn^{4+} is reduced to $\text{Mn}^{3.5+}$. For the subsequent deep insertion, the sodiation exerts a strong destructive effect on the tunneled structure of α - MnO_2 that leads to fast tunnel degradation and phase transition, while the lithiation causes little tunnel degradation up to Mn^{3+} . The difference in charge carrier (Na^+/Li^+) insertion mechanisms should be ascribed to Na^+ 's bigger ionic size and the resulted stronger interaction with the host structure than that of Li^+ .

This work clarifies the underlying charge storage mechanisms when manganese oxides (α - MnO_2) are utilized as NaIB electrodes. Although MnO_2 -based electrode has not been reported to give the best performance among various reported electrode candidates,

we believe that the interaction mechanisms between inserted Na⁺ (Li⁺) and the host structure discovered in this work can help to further improve the electrochemical performance of these materials by proper structure engineering and chemical modification.

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Figure 1. (a,b) [010] Bright field TEM image of one α -MnO₂ nanowire with its corresponding SAED; scale bar: 50 nm; (c,d) [010] HAADF STEM image of the α -MnO₂ nanowire with the atomic model given, where red is for Mn, blue for O and green for K; scale bar: 1 nm; (e) [001] TEM image of one cross sectioned α -MnO₂ slice with the SAED given in the inset; scale bar: 10 nm; (f) [001] HAADF STEM image showing the atomic tunneled structure. One 2×2 tunnel is highlighted by red dots standing for Mn atomic columns and the atomic model is given in the inset. Scale bar: 1 nm.

Figure 2. (a) The *in situ* open cell design inside TEM chamber showing one α -MnO₂ nanowire being sodiated; (b-e) The corresponding SAED patterns from the four predefined sections in (a).

Figure 3. (a) The measured diameter versus sodiation time for one α - MnO_2 nanowire being repetitively cycled; the numeric percentages are for the diameter expansion (positive) and contraction (negative) during each event; (b-g) the corresponding SAED patterns of the same nanowire at different (de)sodiation states.

Figure 4. (a) Normalized XANES spectra of one NaIB with α -MnO₂ nanowire electrode and standard Mn, MnO, Mn₂O₃ and MnO₂; (b) Charge-discharge profile and the oxidation state of Mn during battery cycling.

Figure 5. (Panel A) The EDS maps of Mn and K for a partially lithiated K_{0.25}MnO₂ nanowire; the atomic ratio of Mn and K from the fully inserted nanowire is given at the bottom; (Panel B) The EDS maps of Mn, K and Na for a partially sodiated K_{0.25}MnO₂ nanowire with the atomic ratio of K/Mn given at the bottom; (Panel C) The schematic showing the phase evolution of α -MnO₂ nanowire electrode at different states of discharge (SOD) during lithiation¹⁸ and sodiation.

Graphical Abstract

Authors Biographies:

Yifei Yuan

Mr. Yifei Yuan is a Ph.D. candidate in Michigan Technological University and a visiting scholar at University of Illinois at Chicago advised by Dr. Reza Shahbazian-Yassar. His research interest is *in situ* microscopy of energy storage behaviors of battery materials at single particle level. He is also a guest graduate student studying at Argonne National Laboratory under the supervision of Dr. Jun Lu, and focuses on electrochemical characterization at coin cell level. Yifei obtained both his bachelor (2009) and master (2012) degrees in Materials Science and Engineering from Shandong University in China.

Lu Ma

Lu Ma is currently a PhD candidate in Department of Chemistry and Biochemistry at the Ohio State University. She is now a guest graduate student in Advanced Photo Source, Argonne National Lab under the supervision of Dr. Tianpin Wu. She received her B.S. in Materials Physics and Physical Science (with Honors) from University of Science and Technology of China (USTC) in 2011. Her current research is mainly focused on characterization of battery materials and Mo-S clusters.

Kun He

Miss Kun He is a graduate student in Shandong University. She also worked as a visiting scholar at Michigan Technological University and University of Illinois at Chicago from 2013 to 2015. Her research interest is *in situ* microscopy of solution-based biomineralization process and chemical reactions happening at nano and micro level. She received her Bachelor and Master degrees in Shandong University.

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Wentao Yao is currently pursuing his Ph.D. degree in the department of Mechanical Engineering-Engineering Mechanics at Michigan Technological University. He received his Master degree in materials science from University of Science & Technological Beijing in 2009. His research interests include the hydrothermal synthesise and growth mechanism study of single phase nanowires for high performance lithium/sodium ion battery electrodes, and the effect of grain defects on the diffusion of lithium/sodium ions inside the battery electrode.

Anmin Nie

Anmin Nie received his Ph.D. in Solid Mechanics from Zhejiang University in 2012. During 2012-2014, he worked at the Michigan Technological University as a postdoctoral research associate. Currently, he is a senior research associate in the group of Prof. Reza Shahbazian-Yassar at the University of Illinois at Chicago. His research interests are *in situ* microscopy on nano-scaled materials in liquid and ambient conditions for applications in energy storage.

Xuanxuan Bi

Xuanxuan Bi is a graduate research assistant in Chemistry at the The Ohio State University under the supervision of Dr. Yiying Wu, and a guest graduate at Argonne National Lab under the supervision of Dr. Jun Lu. She received her Master Degree in Chemistry from The Ohio State University in 2015. Her research focuses on the development of the electrode materials for battery technologies and the fundamental study on the battery chemistries.

Khalil Amine

Dr. Khalil Amine is a Distinguished Fellow and the Manager of the Advanced Battery Technology programs at Argonne National Laboratory, where he is responsible for directing the research and development of advanced materials and battery systems for HEV, PHEV, EV, satellite, military and medical applications. Dr. Amine currently serves as a member of the U.S. National Research Council on battery related technologies. Among his many awards, Dr. Khalil is a 2003 recipient of Scientific America's Top Worldwide Research 50 Research Award, a 2009 recipient of the US Federal Laboratory Award for Excellence in Technology Transfer, and is the five-time recipient of the R&D 100 Award, which is considered as the Oscar of technology and innovation. In addition, he was recently awarded the ECS battery technology award and the international battery association award. Dr. Amine holds or has filed over 130 patents and patent applications and has over 280 publications. From 1998-2008, Dr. Amine was the most cited scientist in the world in the field of battery technology.

Tianpin Wu

Dr. Tianpin Wu is the beamline scientist working at beamline 9-BM of the Advanced Photon Source, Argonne National Laboratory. Her expertise is in energy storage and catalyst materials characterization by X-ray Absorption Spectroscopy. She received her undergraduate degree in Chemistry from the Univ. of Science and Technology of China, and her Ph.D. degree in Physical and Analytical Chemistry from the Univ. of Utah. Following two and half years of postdoctoral research in the Division of Chemical Sciences and Engineering at Argonne National Laboratory, she joined the X-ray Science Division as an assistant physicist in 2012.

Jun Lu

Dr. Jun Lu is a chemist at Argonne National Laboratory. His research interests focus on the electrochemical energy storage and conversion technology, with main focus on beyond Li-ion battery technology. Dr. Lu earned his bachelor degree in Chemistry Physics from University of Science and Technology of China (USTC) in 2000. He completed his Ph.D. from the Department of Metallurgical Engineering at University of Utah in 2009 with a major research on metal hydrides for reversible hydrogen storage application. He is the awardee of the first DOE-EERE postdoctoral fellow under Vehicles Technology Program from 2011-2013. Dr. Lu has authored/co-authored more than 130 peer-reviewed research articles and has filed over dozen patents and patent applications.

Reza Shahbazian-Yassar

Dr. Reza Shahbazian-Yassar is an associate professor of Mechanical Engineering at the University of Illinois at Chicago. He received his PhD in Materials Science from Washington State University in 2005. Prior to joining Michigan Tech, he was a post-doctoral research fellow at the Center for Advanced Vehicular Systems at Mississippi State University. He received the Young Leaders Award from TMS in 2015 and was the recipient of 2014 Summer Faculty Fellow from Air Force Research Laboratory. He has published more than 70 journal papers and 4 book chapters. He is a member of steering committee for Nanoengineering for Energy and Sustainability, the current Materials Science Director for Midwest Microscopy Society, and the former chair of the Advanced Characterization, Testing, and Simulation (ACTS) Committee at The Materials Society (TMS). He is also a member of Editorial Board for Journal of Nanotechnology and Smart Materials (JNSM) and Metallurgical and Materials Transactions A (MMTA).