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Progress Report - Keystone 3

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1.1.6.609 Innovation Center for Battery500 – Jun Liu (PNNL) and Yi Cui (Stanford University)

Innovation Center for Battery500

PROJECT OBJECTIVE: The project aims to develop commercially viable lithium (Li) battery technologies with a cell level specific energy of 500 Wh/kg through innovative electrode and cell designs that enable the extraction of the maximum capacity from advanced electrode materials. In addition to achieving high specific energy the project aims to be able to achieve 1000 cycles for the developed technologies.

PROJECT IMPACT: The Battery500 Consortium will develop the next generation Li battery technologies that will significantly increase the energy density, improve the cycle life and reduce the cost. This will greatly accelerate the deployment of electrical vehicles and reduce carbon emission associated with fossil fuel consumption. The consortium will utilize first class expertise and capabilities in battery research in the United States and develop an integrated and multidisciplinary approach to accelerate the development and deployment of advanced electrode materials in commercially viable high energy batteries. The advances made in this consortium will also benefit the improvement of current Li-ion battery technologies.

APPROACH: This project will utilize an assortment of national resources located at the national laboratory and university members. The Li anode combined with a compatible electrolyte system and two cathodes—one high Ni $LiNi_xMn_yCo_zO_2$ (NMC) and another sulfur (S)—will be studied and developed to reach high energy density. The project focus is to design novel electrode and cell architectures in order to meet the 500 Wh/kg goal. The consortium will work closely with R&D companies, battery/materials manufacturers and end-users/OEMs to ensure that the developed technologies are aligned with industry needs and can be transitioned to production.

OUT-YEAR GOALS: Complete first phase full cell fabrication and testing based on the consortium recommended protocols, demonstrating 300 Wh/kg full cell capacity, and provide analytical results for materials selection, cell design and fabrication, and further refinement for 2017. Complete the selection and launching of seedling projects for Batery500.

COLLABORATIONS: The collaboration among team members of this consortium will be well coordinated by the Leadership Team which includes the Keystone Project Leads/co-Leads and PIs at all member institutions. The collaboration with the community outside of this consortium and with industry will be facilitated by the Executive Committee, the Advisory Board and the Industry Committee.

Milestones

1) Complete the establishment of baseline cathode materials, anode materials, electrolytes and cell architecture; establish and implement project plans for all PIs and institutions. (Dec-16). **Completed**
2) Complete the preliminary testing of electrode materials with controlled architectures. Complete the first synthesis of high Ni NMC material, with a specific capacity of 200 mAh/g, and bench mark with NMC622 materials from other groups. (Mar-17) **Completed.**
3) Complete the development of electrolyte formulation for Li deposition with the stable oxidation voltage over 4.3 V and over 98% coulombic efficiency. (Jun-17) **In progress**
4) Complete the construction of 1 Ah pouch cell with 300 Wh/kg specific energy, and over 50 cycles and continuing. Complete the preliminary testing protocol (Sep-17) **In progress**

Progress Report

In the second quarter of FY2017, the second milestones for FY2017 had been completed. The preliminary testing of electrode materials with controlled architectures has been completed. The first batch of high Ni NMC material, with a specific capacity of 200 mAh/g had been synthesized, the electrochemical performance and specific capacity is comparable or better than the bench marked NMC622 materials obtained from commercial sources. The Al doping and surface coating of Al containing materials have been used to improve the high Ni content NMC materials (NMC622, NMC811, and NMC90505). Our results show that such Al doping and Al_2O_3 coatings play critical roles in the capacity retention. In the second quarter of FY2017, the whole consortium team has been continuously working on building research teams, developing research plans and establishing baseline cathode materials. The roles and responsibilities of the Leadership Team have been refined. A total of 14 projects are defined. A Working Committee, made of one representative from each institution was formed with the function of keeping the whole consortium updated of the research progresses through biweekly telephone conferences. In the second quarter, several large core groups, including the NMC cathode group, the Li metal anode group, and the S group have been formed. The coordinator for each large core group is responsible for organizing biweekly phone conferences to exchange research results and discuss important issues within each project throughout the whole second quarter. These teleconferences were also announced through the whole consortium to welcome PIs, research scientists, postdocs, and students from other project to attend and provide their inputs. In addition, several sub-groups were also formed, including the electrolyte group, the characterization group, the diagnostic and electrochemical characterization group, and the cell design and fabrication group. These subgroups are responsible for ensuring regular communications and meeting program goals on the project level. More detailed discussions were followed up after each tele-conference, especially among the young scientists in each group. At many tele-conferences, the young scientist (postdocs and students) are the main presenter and their active involvement during and after the tele-conference is the key factor to achieve the milestone for Q2 of FY2017. The FY2017 second quarterly review meeting was held at University of Texas at Austin from April 27 to 28, 2017. About 40 people attended that review meeting, including the Executive committee members, DOE representatives (David Howell, Tien Duong, Jack Deppe, and Patricia Smith). Besides all the PIs and some staff scientists from each institution, many postdocs and graduate students, especially from local institutions also attended this review meeting, greatly encouraged the participation of young scientists of this program. David and Tien each gave a talk about the VTO and BMR update. The program director Jun Liu gave an overview. A total of 12 other presentations were given by the project leaders and PIs. It was a very successful review meeting. Another bright spot of this Q2 review meeting is the poster session presented by the young scientists. Very interesting discussions, questions and answers among the presenters and other attendees took place during the poster session. It was suggested that we should have longer time for poster session in our future quarterly reviewer meetings.

For the technique part is devided by the three Keystone projects in the following pages.

Q2 report for Keystone Project 1

On high-Ni NMC cathodes, the baseline materials of NMC622 and NMC811 from commercial source (EcoPro) were first characterized. Figure 1a and b shows the effect of the active material loading on the electrochemical perfomance of both commercial 622 and 811 at different current densities, respectively. EcoPro NMC622 shows high dependence of rate performance on sample loading, and high loading leads to poor electrochemical performance at higher rates. However, the NMC811 does not show significant electrochemical dependence on loading. However, we observed hints of the formation of a second phase at above 4.2 V in NMC811 (Figure 1c, blue curves). The NMC622 material has also been prepared in-house and it shows comparable results to the commercial 622 material (Figure 1c, black and red lines).

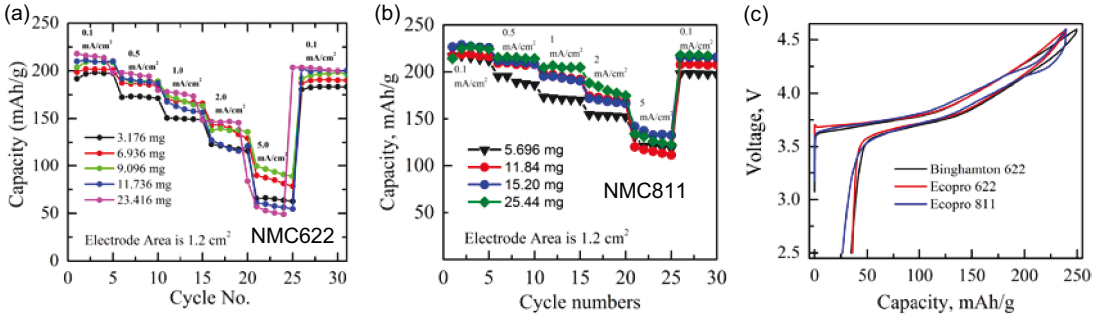

Figure 1. Rate capability test of the EcoPro NMC622 (a) and NMC811 (b) at different loadings and comparison of electrochemical perfomance of in-house synthesized NMC622 to the baseline 622 and 811 EcoPro samples (c).

High-Ni NMC materials with Ni content of 60~94% have also been synthesized in house and characterized. These show the desired meatball morhology (Figure 2a) with very uniform particle sizes. The electrochemical performance indicates as expected that the higher Ni contents lead to higher capacities (Figure 2b). The in-house materials also show good cycling stability in full cells except for the 90% Ni NMC (Figure 2c). Al-doping in the high-Ni NCO greatly enhances the cycling stability (Figure 2d). In addition, using $LiAlO_2$ to coat on NMC622 can also stabilize the cycling stability.

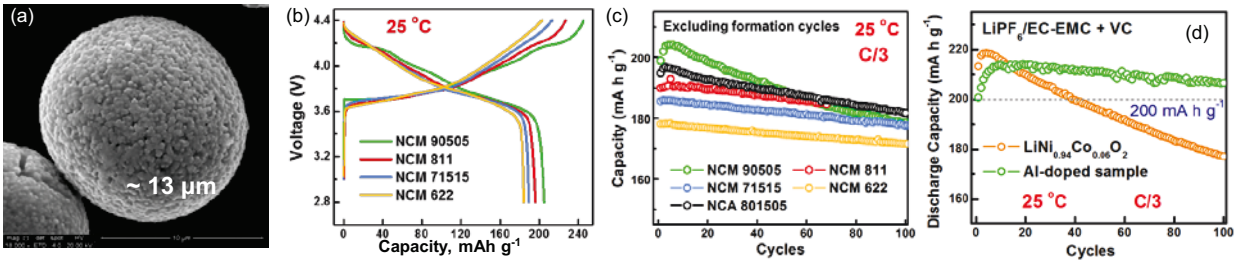

Figure 2. Morphology of the in-house synthesized high-Ni NMCs showing spheres with the primary and secondary particles in the meatballs (a), and electrochemical performances of first cycle votage profiles (b) and cycle life (c) in graphite||NMC full cells between 4.4 and 2.8 V. (d) Comparison of cycling performance of high-Ni $Li_{0.94}Co_{0.0}6O_2$ with and without Al-doping in half cells.

On Li metal anodes, 3D structured Li/carbon cloth composite anode has been developed and shows good rate capability and cycling stability in Li||NMC622 cells. Core−shell nanoparticle coating has been prepared as an interfacial layer for dendrite free Li metal anodes. An adaptive “solid-liquid” interfacial layer was also developed to protect Li metal anode. In addition, a robust coating layer of crystalline methyl lithium carbonate was formed in-situ on Li metal surface through a solution chemical process and dendrite free Li metal anode was observed after long-term cycling at 3 mA cm^{-2} in conventional $LiPF_6$/carbonate based electrolyte.

Q2 report for Keystone Project 2: Electrode Architectures

The goal of the Keystone 2 is to design, model, fabricate and characterize the effect of electrode architecture on electrode and cell performance in support of reaching the project of 500 Wh/kg cell specific energy. Included in this Keystone are architecture design of thick cathodes (UCSD), lithium metal electrode architectures (PNNL and Stanford), inorganic (UT-Austin) and polymer (Stanford) electrolytes, and electrode performance modeling (UW).

Cycling performance of the baseline NMC622 material was measured as a function of type and amounts of binder, carbon, and active material loadings. A new electrode architecture with high amount of straight voids in the electrode was fabricated. Electrochemical impedance measurement confirmed a reduction of tortuosity (**Figure 1a**). Modeling of an electrode with graded porosity shows improved power capability as well **(Figure 1b**). These two examples show the potential of designing electrode architectures to achieve higher power density.

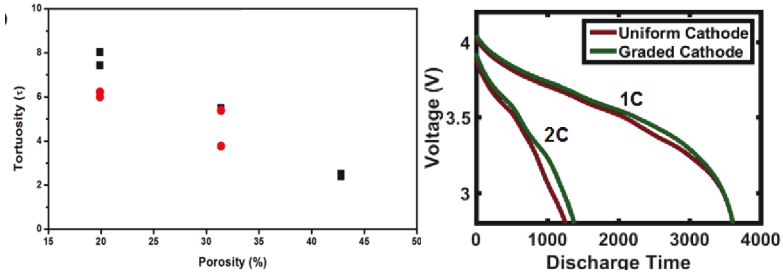

Figure 1. (a) Tortuosity as a function of porosity (red and black symbals correspond to two sets of electrodes with different architectures); (b) Modeled discharge curves for a uniform cathode and a cathode with grade porosity through its thickness (higher porosity near the surface)

Electrode design for lithium anode has focused on developing 3D hosts for lithium deposition which reduce effective current density and maintain macroscopic dimension, both of which promise longer cycle life. A Li-NMC cell has shown excellent cycling stability and rate performance when using a 3D conducting structure for lithium deposition (Figure 2a). Another method to control lithium deposition is through the use of a flowable, highly viscoelstic polymer coating which promotes more uniform nucleation of lithium (Figure 2b and c). Further, new polymer electrolytes were designed to offer higher ion conductivities and stable interface with lithium by manipulating the lithium ion coordination environment. Finally, a solid electrolyte $Li_{3/8}Sr_{7/16}Hf_{1/4}Ta_{3/4}O_3$ (LSHT) has shown a room temperature conductivity of 3.8×10^{-4} S cm^{-1} at 25 °C and demonstrated good stability with lithium metal.

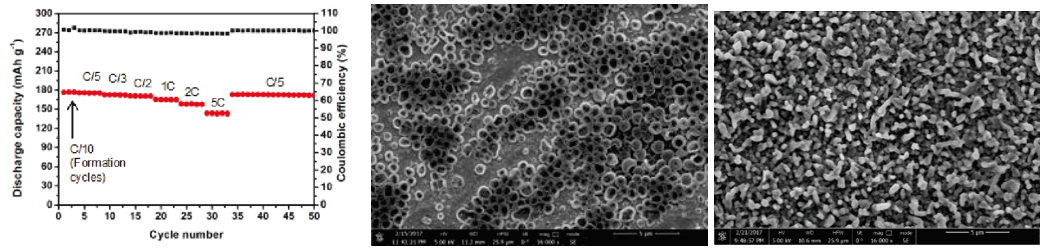

Figure 2a-c (left to right). (a) capacity retention of a Li-NMC622 battery with a lithium anode where lithium is deposited in a designed 3D structure; (b and c) scanning electron micrographs of lithium deposited on bare copper (b) and on copper coated with flowable polymer.

In summary, all elements of the Keystone are progressing towards the goal of a high energy cell with stable lithium metal anode and a thick, high energy cathode. Work continues in further development of electrode architectures guided by modeling and with increased coordination with the Characterization team in the Consortium to understand the mechanisms of performance improvement.

Q2 report for Keystone Project 3

In the second quarter of FY2017, the focus of Keystone 3 was jointly on the establishment of methods for evaluation of high energy cells both electrochemically and through the use of advanced characterization techniques and resources, establishment of methods for the preparation of 1 Ah or larger cells, and use of different models to identify cell design parameters for achieving both 300 and 500 Wh/kg. These routes directly support the fourth quarter milestone in FY17 of achieving 300 Wh/kg and the ability to cycle the cell a minimum of 50 times. To facilitate discussions between the Keystone 3 team members biweekly meetings have been held to discuss path and to ensure progress is moving forward.

Performing analysis of fade which occurs during cycling provides a pathway to identify gaps which are emerging in cell design. This gap identification enables other keystone areas to then refine materials or designs to improve performance. During the second quarter of FY17 efforts to understanding fade using standard test practices were evaluated. As part of the process, differential capacity (dQ/dV) analysis was performed to understand how materials in both the positive and negative electrode were performing. Figure 1 shows a representative cell that as it ages over 50 cycles shows distinct changes in performance. Through analysis of the data in the figure and other corresponding data it was possible to identify that while the capacity was fading that a significant aspect of the fade was not due to the positive electrode (NMC 622) performance, but was instead associated with the ability of the Li metal negative electrode. As an analysis method dQ/dV and other metrics developed thus far will be applied to the cells which will be part of the fourth quarter milestone for FY17. To prepare for this activity a full flow chart has been developed. Currently progress in preparing cells of at least 1 Ah is on pace for delivery of cells prior to Q4.

One of the other key areas of interest during Q2 for Keystone 3 was on identifying parameters which will enable optimization of both cell performance and energy density. This will help enable the Battery500 project to advance from the initial cell development at 300 Wh/kg to the final 500 Wh/kg. Key parameters which are being evaluated include electrode thickness, porosity, tortuosity and overall loading of active high Ni NMC materials or of sulfur. Initial bounds for each parameter have been identified and are being refined to understand the full sensitivity of the parameters on overall cell design. In conjunction with parametric analysis, models looking at how to more effectively define a Li metal battery have been established. Figure 2A includes the general premise for the initial model which includes a porous positive electrode and a planar Li metal negative electrode. A key component of the Li metal side of the cell is that a moving boundary is included. Figure 2B includes predicted values using this model and experimental data collected for a cell that had an NMC 622 positive electrode. With the inclusion of the moving boundary good agreement between model and experiment have been identified.

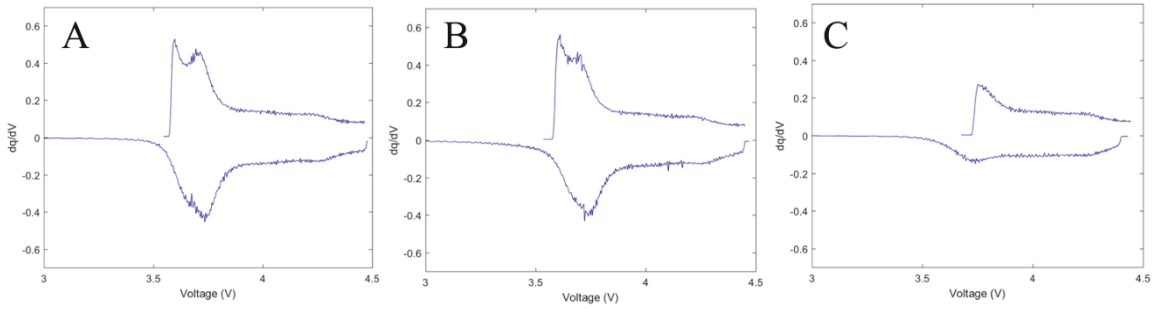

Figure 1: Differential capacity plots for an NMC 622 cell with a Li negative electrode. As the cell ages distinct aging mechanisms emerge which can be related to the Li metal. A) Initial B) After 25 cycles at C/3 C) After 50 cycles

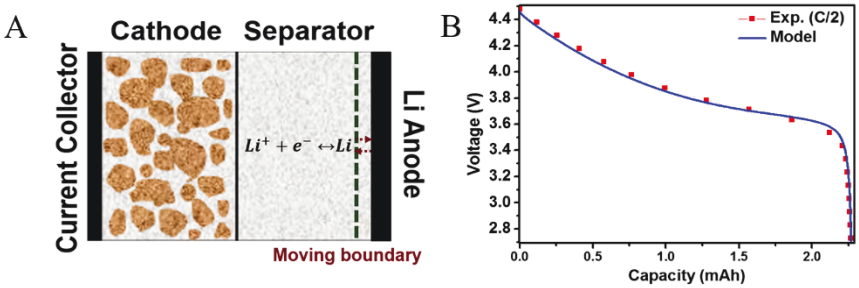

Figure 2: A) Schematic of modelled system B) Comparison between model and experimental data for a NMC 622 cell.

Patents/Publications/Presentations

Publications:

1. Yahong Xu, **Enyuan Hu**, Kai Zhang, **Xuelong Wang**, Valery Borzenets, Zhihong Sun, Piero Pianetta, Xiqian Yu, Yijin Liu, **Xiao-Qing Yang***, Hong Li, "In-situ Visualization of State-of-Charge Heterogeneity within a $LiCoO_2$ Particle that Evolves upon Cycling at Different Rates", *ACS Energy Letter*, 2017, In press.
2. **J. Zheng, M. H. Engelhard, D. Mei, S. Jiao, B. J. Polzin, J.-G. Zhang, W. Xu**, "Electrolyte Additive Enabled Fast Charging and Stable Cycling Lithium Metal Batteries", *Nature Energy*, 2017, 2, 17012.
3. **D. Lin, Y. Liu,** and **Y. Cui**, "Reviving the lithium metal anode for high-energy batteries", *Nature Nanotechnology* 12, 194-206 (2017).
4. **A. Pei, G. Zheng, F. Shi, Y. Li,** and **Y. Cui**, "Nanoscale Nucleation and Growth of Electrodeposited Lithium Metal", *Nano Letters* 17, 1132–1139 (2017).
5. **W. Liu, W. Li, D. Zhuo, G. Zheng, Z. Lu, K. Liu,** and **Y. Cui**, "Core-Shell Nanoparticle Coating as an Interfacial Layer for Dendrite-Free Lithium Metal Anodes", *ACS Central Science* 3, 135-140 (2017)
6. **K. Liu, A. Pei, H. R. Lee, B. Kong, N. Liu, D. Lin, Y. Liu, C. Liu, P.-C. Hsu, Z. Bao,** and **Y. Cui**, "Lithium Metal Anodes with an Adaptive 'Solid Liquid' Interfacial Protective Layer", *Journal of the American Chemical Society* 139, 4815–4820 (2017)
7. **W. Li, A. Dolocan, P. Oh, H. Celio,** and **A. Manthiram**, "Dynamic behavior of interphases and its implication on high-energy-density cathode materials in lithium-ion batteries," *Nature Commun*ications **2017**, 8, 14589.
8. **W. Li, B. Song,** and **A. Manthiram**, "High-voltage positive electrode materials for lithium-ion batteries," *Chemical Society Reviews, DOI: 10.1039/C6CS00875E*
9. **W. Li, U.-H. Kim, A. Dolocan,** Y.-K. Sun**,** and **A. Manthiram**, "Formation and Inhibition of Metallic Lithium Microstructures in Lithium Batteries Driven by Chemical Crossover," ACS Nano (submitted).
10. **S. B. Lee, C. Pathak, V. Ramadesigan, W. Gao,** and **V. R. Subramanian**, "Direct, efficient, and real-time simulation of physics-based battery models for stand-alone PV-battery microgrids", J. Electrochem. Soc, 164 (11), E3026-E3034 (2017).

Note: The author names in bold font are fully or partially supported by Battery500 consortium

Invited presentations:

1. **Xiao-Qing Yang**, "Studies of New Electrode Materials for Next Generation of Batteries Using Synchrotron Based In situ X-ray Diffraction and Absorption as well as TXM Techniques", Presented at International Battery Association IBA2017 meeting, Nara, Japan, March 5-10, 2017.
2. **M. Stanley Whittingham**, "The Limits of High Energy Reactions for Lithium Batteries: The Electrolyte Challenge", Presented at International Battery Association IBA2017 meeting, Nara, Japan, March 9th 2017.
3. **M. Stanley Whittingham**, "Electrical Energy Storage: Where have we come from and the scientific challenges still facing us", presented at US DOE Basic Research Needs Workshop, Gaithersburg, MD, March 27th 2017.
4. **K. Adjemian, B.Y. Liaw**, "The grand challenge of advanced batteries." Presented at The 34th International Battery Seminar and Exhibit, Fort Lauderdale, FL, March 20-23, 2017.
5. **B.Y. Liaw**, "Enable a viable pathway toward battery durability, reliability and safety." Presented at International Battery Association IBA2017 meeting, Nara, Japan, March 5-10, 2017.
6. **B.Y. Liaw**, "A viable pathway from durability to reliability and safety." Energy Storage Safety Forum, Santa Fe, NM, February 22-24, 2017.
7. **Jun Liu,** KEYNOTE LECTURE, "Emerging Technologies for Transportation and Grid Scale Storage", Presented at International Battery Association IBA2017 meeting, Nara, Japan, March 5-10, 2017.
8. **Yi Cui**, Plenary, "Nanomaterials Design for Energy" International Conference on Materials for Energy Applications, City University of Hong Kong, Jan 3-6, 2017.
9. **Yi Cui**, "Reviving Lithium Metal Anode Through Materials Design", HKUST-Argonne National Lab Workshop on Energy Storage Systems, Jan 4, 2017, Hongkong University of Science and Technology.
10. **Yi Cui**, "Nanomaterials Design for Energy and Environment" Institute of Textiles and Clothing seminar, Hongkong Polytech University, Jan 6, 2017.
11. **Yi Cui**, (Keynote) "Reviving Lithium Metal Anode Through Materials Design", The International Battery Association (IBA) 2017 Meeting, Nara, Japan, March 5-10, 2017.
12. **Michael Toney**, "Mechanistic Insights into Energy Storage from X-ray Scattering", National Renewable Energy Laboratory Seminar, March 3, 2017.
13. **Michael Toney**, "Mechanistic Insights into Energy Storage from X-ray Scattering and Spectro-Microscopy", Materials Sciences and Engineering Colloquium, Stanford University, Feb 3, 2017.
14. **Michael Toney**, "Operation of sustainable energy materials", IBM Almaden Research Center Colloquium, 1/13/2017.
15. **Michael Toney**, "Mechanistic Insights into Energy Storage from X-ray Scattering", Argonne National Laboratory, Materials Sciences and Chemical Sciences Divisions Joint Colloquium, 1/12/2017.
16. **W. C. Chueh**, "Opportunities in Challenges in Developing Materials for Lithium-Ion Batteries", American Chemical Society National Meeting. San Francisco, USA. Apr. 4, 2017.

17. **W. C. Chueh**, "Opportunities in Challenges in Developing Materials for Lithium-Ion Batteries", Rice University, Materials Science & NanoEngineering. Houston, USA. Mar. 30, 2017.
18. **Y. Shirley Meng** – KEYNOTE TALK "Pushing the Limit of Intercalation Compounds - a comparison between classical layered oxides and lithium-excess layered oxides", Presented at International Battery Association IBA2017 meeting, Nara, Japan, March 5-10, 2017.