EFRC: NORTHEAST CENTER FOR CHEMICAL ENERGY STORAGE (NECCES)

UPDATED: AUGUST 2016

AWARDS: $17M (August 2009 – July 2014); $13.3 M (August 2014 – July 2018	
WEBSITES: http://science.energy.gov/bes/efrc/centers/EFRC/; http://necces.binghamton.edu	
TEAM: **Binghamton University (Lead):** M. Stanley Whittingham (Director), Louis Piper, Guangwen Zhou, Natasha Chernova; **Argonne National Laboratory**: Karena Chapman, Peter Chupas; **Massachusetts Institute of Technology**: Yet-Ming Chiang; **Rutgers, The State University of New Jersey:** Glenn Amatucci, Frederic Cosandey, Philip Batson, Natalie Pereira; **University of Cambridge:** Clare Grey; **University of California, Berkeley:** Gerbrand Ceder; **University of California, San Diego:** Shirley Meng, Shyue Ping Ong; **University of California, Santa Barbara:** Anton Van der Ven; **University of Illinois at Chicago:** Jordi Cabana; **University of Michigan:** Katsuyo Thornton	

SCIENTIFIC MISSION AND APPROACH

The mission of NECCES is to develop an understanding of how key electrode reactions occur in cathode materials for Li based batteries, and how they can be controlled to improve electrochemical performance, from the atomistic level to the macroscopic level through the life-time of the operating battery. This mission will allow the determination of the ultimate limits of intercalation reactions for chemical energy storage. The approach and specific research goals of NECCES are to:

1. Attain reversible multi-electron transfer in a cathode material using lithium, using the model compound ε -$VOPO_4$.
2. Close the gap between the theoretical and practical energy density for intercalation compounds, using the model compound $LiNi_{0.85}Co_{0.10}Al_{0.05}O_2$.
3. Understand performance limiting transport in positive electrode structures from the local through the meso to the macroscale.

To attain these research goals the center is divided into three closely connected and integrated thrusts; the theory effort is integrated into thrusts 1 and 2.

Thrust 1. Intercalation Materials Chemistry: Identify the key materials parameters that are required to optimize intercalation reactions in the bulk active material itself.

Thrust 2. Electrode Transport - Establishing the Local-Meso-Macro Scale Continuum: Establish a comprehensive understanding of the ionic and electronic transport in full electrodes.

Thrust 3. Cross-Cutting Diagnostics: Develop novel *operando* experimental approaches to allow a full understanding of all the reactions occurring in battery materials.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Showed using a combination of theory and experiment that lithium intercalation in the high rate nanosized Olivine $LiFePO_4$ occurs by a metastable single phase reaction.
- Developed the AMPIX cell that allows meaningful operando measurements in electrochemical cells, and used it for elucidating complex structures formed during electrochemical reactions.
- Showed that 2 Li can be reversibly intercalated into a host lattice in a reversible manner, and predicted the most stable phases in the model compound materials Li_xVOPO_4.
- Elucidated the reaction mechanism of conversion cathode materials, such as FeF_y.
- Developed and used NMR tools to reveal type and place of electrodeposited lithium.
- Showed that the charge transfer in layered oxides is a strong function of the lithium content.
- Determined the location and the key roles that Al plays in the layered oxide cathode materials.

NECCES research from left to right: experimental and theoretical profiles of two Li cycling in ε-LiVOPO$_4$, AMPIX cell for in-situ synchrotron studies and techniques employed by NECCES at APS, TEM image and schematic of continuous Fe particle network enabling reversible conversion reaction of FeF$_2$.

IMPACT

- When NECCES was initiated, the cathode material LiFePO$_4$ presented a dichotomy. It was an electrical insulator and a one-dimensional Li ion diffuser, yet exhibited an extremely high lithium intercalation and removal. NECCES showed using a combination of theory and experiment, backed up by *operando* cell studies, that nano-sized LiFePO$_4$ reacts by a single phase mechanism, Li$_x$FePO$_4$, and that so long as a high rate of reaction is taking place the lithium ions remain disordered over the lattice sites rather than ordering to form the two phases, LiFePO$_4$ and FePO$_4$. This understanding is now being applied to the 2 Li material, Li$_2$VOPO$_4$.
- Determined the key parameters controlling and limiting the application of conversion reaction materials, such as FeF$_y$. This understanding is now being applied to the higher energy density CuF$_2$.
- NECCES researchers are recognized as world leaders in developing *operando* techniques to understand electrochemical reactions in solid materials. They have been received numerous international awards, including several for junior and mid-career scientists: the ECS Tobias Award (Shirley Meng), the MRS Outstanding Young Investigator Award (Karena Chapman) and the Chemical & Engineering New's Talented Twelve (Karena Chapman).

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, NECCES had published 139 peer-reviewed publications cited over 4,400 times and filed 11 disclosures, 4 US patent applications, and 2 foreign patent applications. 2 patents have been issued and 1 disclosure or patent application licensed. The following is a selection of impactful papers:

- Malik, R., Burch, D., Bazant, M., and Ceder, G. Particle size dependence of the ionic diffusivity. *Nano Letters* **10** 4123-4127, doi:10.1021/nl1023595 (2012). [**288 citations**]
- Xu, B., Fell, C. R., Chi, M., and Meng, Y. S. Identifying surface structural changes in layered Li-excess nickel manganese oxides in high voltage lithium ion batteries: A joint experimental and theoretical study. *Energy & Environmental Sciences* **4**, 2223-2233, doi:10.1039/C1EE01131F (2011). [**298 citations**]
- Malik, R., Zhou, F., and Ceder, G. Kinetics of non-equilibrium lithium incorporation in LiFePO$_4$. *Nature Materials* **10**, 587-590, doi:10.1038/NMAT3065 (2011). [**210 citations**]
- Wang, F., Robert, R., Chernova, N. A., Pereira, N., Omenya, F. O., Badway, F., Hua, X., Ruotolo, M., Zhang, R., Wu, L., Volkov, V., Su, D., Key, B., Whittingham, M. S., Grey, C. P., Amatucci, G. G., Zhu, Y., and Graetz, J. Conversion reaction mechanisms in lithium ion batteries: Study of the binary metal fluoride electrodes. *JACS* **133**, 18828-18836, doi:10.1021/ja206268a (2012). [**181 citations**].
- Hu, Y-Y., Liu, Z., Nam, K-W., Borkiewicz, O., Cheng, J., Hua, X., Dunstan, M., Yu, X., Wiaderek, K., Du, L-S., Chapman, K. W., Chupas, P. J., Yang, X-Q., and Grey, C. P. Origin of additional capacities seen in metal oxide lithium-ion battery electrodes. *Nature Materials* **12**, 1130-1136, doi:10.1038/NMAT3784 (2013). [**173 citations**]
- Whittingham, M. S. The ultimate limits to intercalation reactions for lithium batteries, *Chemical Reviews* **114**, 11414–11443, doi: 10.1021/cr5003003 (2014). [**122 citations**]
- Chandrashekar, S., Trease, N. M., Chang, H. J., Du, L-S., Grey, C. P., and Jerschow, A. 7Li MRI of Li batteries reveals location of microstructural lithium. *Nature Materials* **11**, 311-315, doi:10.1038/nmat3246 (2012). [**105 citations**]