

Thrust Area 4: Solar (PV Integration) ***Integrated PV/Storage and PV/Storage/Lighting Systems***

PI: Franky So **Co-PIs:** Jiangeng Xue, Shirley Meng
Students: Ming-Che Yang/ PhD candidate;
Chris R. Fell/PhD candidate; Fred Steffy/MS candidate;
William Hammond (PhD candidate); Edward Wrzesniewski (PhD candidate)

Description: The goal is to increase the efficiency and reduce the cost of solar power through the integration of PV, Li-battery, and LED lighting technologies. Since all components are in the form of thin films, the PV/battery/LED system can be integrated as a single module. Since half of the materials cost of each device is the substrate, integrated module will also reduce materials costs and processing steps. Importantly, their integration further eliminates the need for inverters since they are all low-voltage devices. Such an integrated device can be used to store energy during the day and power the LED panel for lighting in the evening. In addition, we will explore the possibility of fabricating a semi-transparent module. The success of this Task will lead to a novel solar-power lighting panel that can be used as a sky light during the day and a lighting panel during the night without using grid-power. We not only will develop the technologies, but also integrate devices and perform technology-economic evaluation, including life-cycle costs.

Budget: \$576,000

Universities: UF

External Collaborators: University of California San Diego, Oak Ridge National Lab

Project Summary

In the area of lighting and photovoltaics, we focused on light management and hybrid light emitting and PV devices. We have made use of “defective” grating structures to extract thin film guided modes in OLEDs. Because of the lack of long range ordering, we were able to achieve lambertian-like emitters with a 2X enhancement in light output. We have also developed novel optical structures for enhancing the efficiency of organic and hybrid organic-inorganic photovoltaic cells by allowing the active materials to more efficiently absorb the incident light. Two different optical structures were created and applied to the PV cells using a soft lithographic process, which could be easily implemented in large-scale high throughput manufacturing systems. Such enhancement mechanism could also be universally applied to any active materials or device platforms. For hybrid solar cells, we have significantly improved the efficiency of hybrid polymer-colloidal nanocrystal solar cells by engineering the chemical and electronic structures at the polymer-nanocrystal interface. This yields a maximum power conversion efficiency of 5%, the highest for solid-state hybrid solar cells. Finally, we also developed fully solution processed, multilayer quantum-dot based light-emitting devices that show high efficiency and full visible spectrum color tunability.

Lithium-ion batteries are efficient, light-weight and rechargeable power sources for consumer electronics such as laptop computers, digital cameras, MP3 players and cellular phones. However, for the use as energy storage component in this proposed work, the energy density, power density safety and cycling performance still can't achieve the requirements. In this research, three different strategies were selected to improve the rate capability, cycling performance and investigate the solid electrolyte interface. First, the first principles computation was used to selected suitable doping metal and proved by real experiment. Second, the TiO₂ nanostructure was synthesized and the electrochemical properties were examined. Finally, the thin film batteries were fabricated by pulsed laser deposition (PLD) and the solid electrolyte

interface were investigated by XPS. In addition, the layered lithium excess layered oxide compounds $\text{Li}[\text{Ni}_x\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}]\text{O}_2$ ($0 < x < 1/2$) are of great interests as a new generation of positive electrode materials for lithium-ion batteries because of higher energy densities and lower costs. However, the rate capabilities of these materials are not adequate for future applications. Preliminary studies have proposed mechanisms to explain this material's anomalous capacity; however the mechanism still remains unclear. In order to break the rate capability barrier, a complete understanding of the lithium diffusion mechanism needs to be understood. We uses a series of characterization techniques to identify the rate limiting step that impedes lithium diffusion and propose new strategy to further improve the electrochemical properties of this new family of electrode materials.

Funds leveraged/new partnerships created:

- Northeastern center for chemical energy storage (NECCES) – a DOE energy frontier research center. Partnership with University of California San Diego (UCSD) and State University of New York (SUNY) at Stony Brook

Grants awarded

Title	Agency	Reference Number	PI, Co-investigators and collaborators	Period of Performance	Funding awarded
Materials and Devices compatible with high volume roll-to-roll manufacturing of polymer solar cells	Office of Naval Reseach		Franky So, John Reynolds and Frederik Krebs	Jan, 2011-Dec, 2013	\$750,000
High efficiency OLEDs for lighting	DOE		Franky So, Nelson Tansu	Jun. 2009-May 2012	\$780,000

Proposals submitted

Proposals (Xue)						
Title	Agency	Reference Number	PI, Co-investigators and collaborators	Funding requested	Project time frame (1 year, 2 years, etc.)	Date submitted
A Modular Supramolecular Approach to Organic Photovoltaic Materials	Research Corporation for Science Advancement		Co-PI	\$250,000	3 years	01/18/11
SOLAR Collaborative: Solar Energy Harvesting Using Photon-Driven Molecular Nanomotor Assembly	NSF		Co-PI	\$1,284,072	3 years	01/28/11
Development of Scalable Bottom-Up Nanomanufacturing Platforms	NSF		Co-PI	\$2,000,000	4 years	01/10/11
Solution-processed, Earth-abundant Semiconductors for High Efficiency Solar Cells	DOE		PI	\$1,500,000	3 years	06/28/11

Light management in organic solar cells and organic light emitting diodes

2. Light extraction using defective grating structure

In collaboration with Dr. Nelson Tansu at Lehigh University, OLEDs were fabricated on grating substrates. These grating substrates were fabricated by coating 1 μm diameter and 0.5 μm SiO₂ microlens array on glass substrates. Fig. 1 shows the AFM images of these microlens arrays along with their power spectral densities obtained from FFTs shown in the insets. The FFTs show that the lack of long range ordering in the arrays. As a result, the light emission profiles of the resulting OLEDs are very similar to a lambertian emitter.

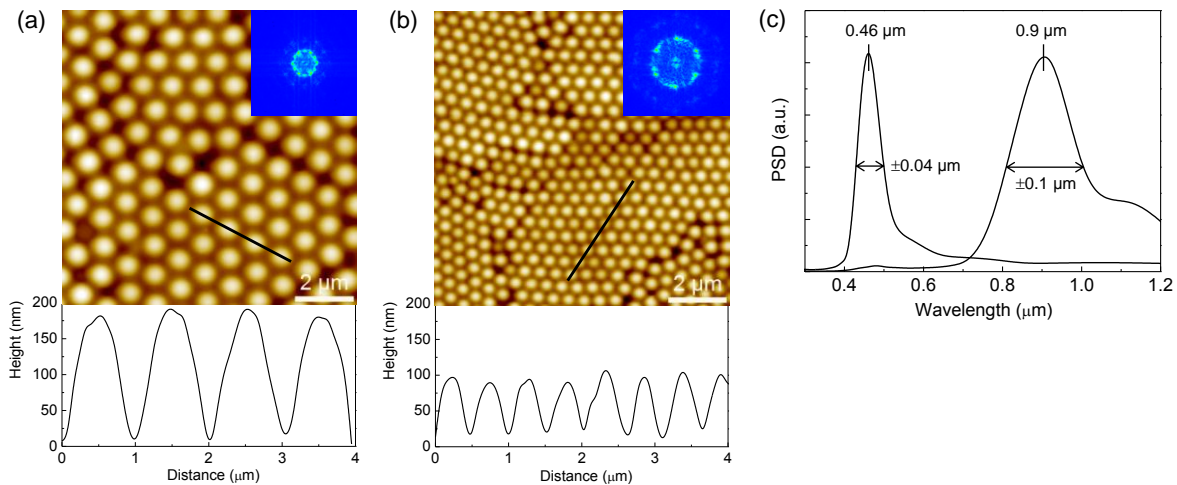


Figure 1: AFM Images Of A 1.0 Mm (A) and 0.5 Mm (B) Substrates. The Power Spectral Densities of the Corresponding Grating Substrates are Shown in (C).

Fig. 2 shows the current efficiency and the power efficiency of OLEDs fabricated on μm grating substrates along with the results of a controlled device. Enhancements of 70% and 100% were achieved for the current and power efficiencies due to the 0.5 μm grating. The larger enhancement of the 0.5 μm grating device compared to the 1.0 μm grating device is associated with the larger grating vector of the 0.5 μm grating.

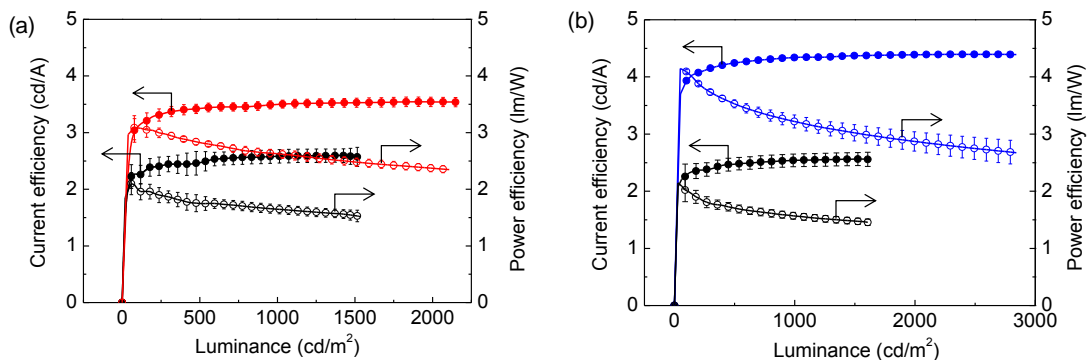


Figure 2: Current and Power Efficiency of Oleds Fabricated on 1 Mm (A) and 0.5 Mm (B) Substrates. The Data for the Control Device are Shown in Black.

2. Optical structures for enhancing light absorption in organic solar cells

We have developed novel optical structures for enhancing the efficiency of organic and hybrid organic-inorganic photovoltaic cells by allowing the active materials to more efficiently absorb the incident light. Two different optical structures were created and applied to the PV cells using a soft lithographic process, which could be easily implemented in large-scale high throughput manufacturing systems. Such enhancement mechanism could also be universally applied to any active materials or device platforms. In one structure, a pyramidal rear reflector structure was molded on a semi-transparent organic solar cell, as shown in Fig. 3(a). The total internal reflection at the device/air interface when the incident light attempts to escape the device leads to significantly increased optical path length in the device. As shown in Fig. 3(c), compared with the normal device with a planar rear reflector, this pyramidal structure could yield a 15-70% increase in the solar cell efficiency, depending on the active layer thickness and the alignment of the device with respect to the pyramid.

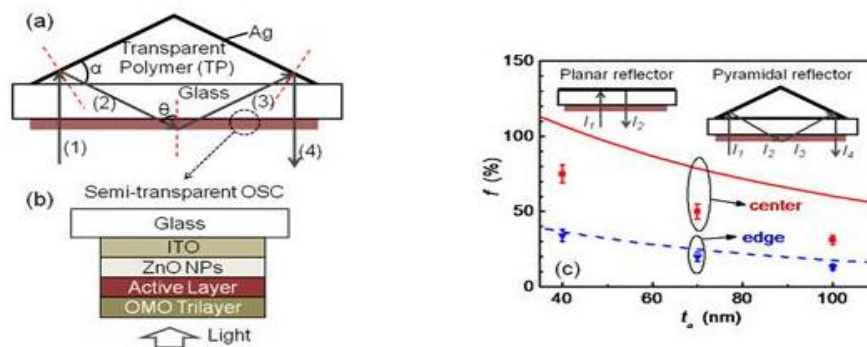


Fig. 3. Schematic illustrations of (a) a pyramidal rear reflector structure and (b) a semi-transparent organic solar cell. (c) shows the efficiency enhancement factor as compared to a device with planar rear reflector.

In the second optical structure, we have applied a molded microlens array (shown in Fig. 2a) to the organic solar cell light incident surface. Figure 4b shows the current density-voltage characteristics of a bilayer SubPc/C₆₀ cell under 1 sun AM1.5G solar illumination, which shows a 20% enhancement in efficiency with the microlens array. Figure 2c shows that by varying the C₆₀ layer thickness, a maximum enhancement of 60% could be achieved.

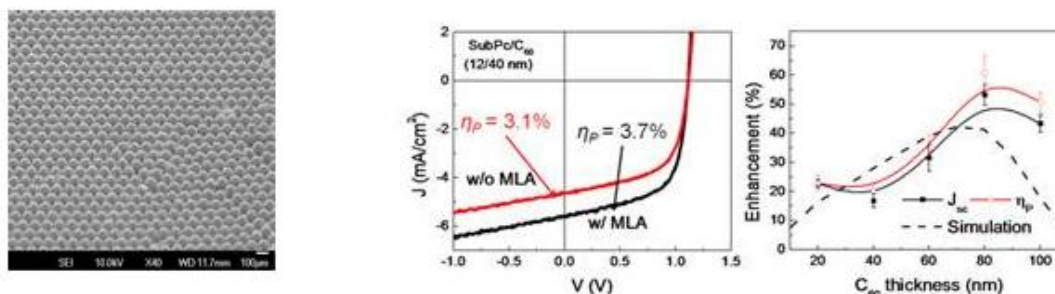


Fig. 4. (a) SEM image of a microlens array (MLA); (b) current density-voltage characteristics of a subPc/C₆₀ bilayer organic solar cell with or without the microlens array; (c) enhancement factor in J_{sc} or efficiency as a function of the C₆₀ layer thickness.

Hybrid polymer-nanocrystal solar cells

We have also greatly improved the efficiency of hybrid polymer-nanocrystal solar cells by applying proper chemical treatment to passivate the surface of the nanocrystals. The passivation leads greatly reduced defect densities on the CdSe nanorods, which otherwise would lead to recombination of photogenerated excitons and/or charge carriers. As shown in Fig. 5, using this treatment process, for hybrid solar cells based on CdSe nanorods and a low-gap polymer PCPDTBT, we obtain a more than 40% increase in the power conversion efficiency, leading to a maximum of ~5.0%, the highest so far achieved for this type of solar cells.

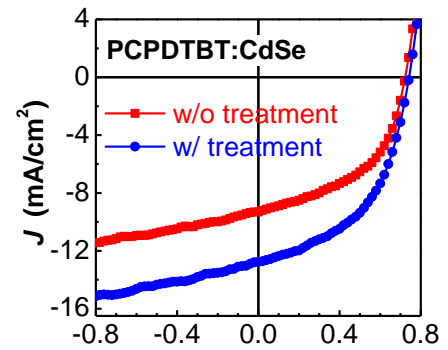


Fig. 5.: The I-V characteristics for PCPDTBT:CdSe nanorod hybrid solar cells with or without the chemical treatment.

Solution processed, quantum-dot based, multilayer light-emitting devices

We successfully fabricated multilayer quantum-dot based light-emitting devices using solution process. The device structure is shown in Fig. 6a where an organic layer poly-TPD acts as hole transport layer, a CdSe-ZnS core-shell quantum-dot layer acts as the light emitting layer, and a ZnO nanoparticle layer serves as the electron transport layer. By tuning the size and composition of the CdSe-ZnS quantum dots, we can achieve tuning of color emission from blue to orange-red (see Fig. 6b). The efficiency of these devices are several times higher than previously reported devices, with a maximum luminous efficiency of ~8 lm/W for the green device and a maximum luminance of over 10,000 cd/m².

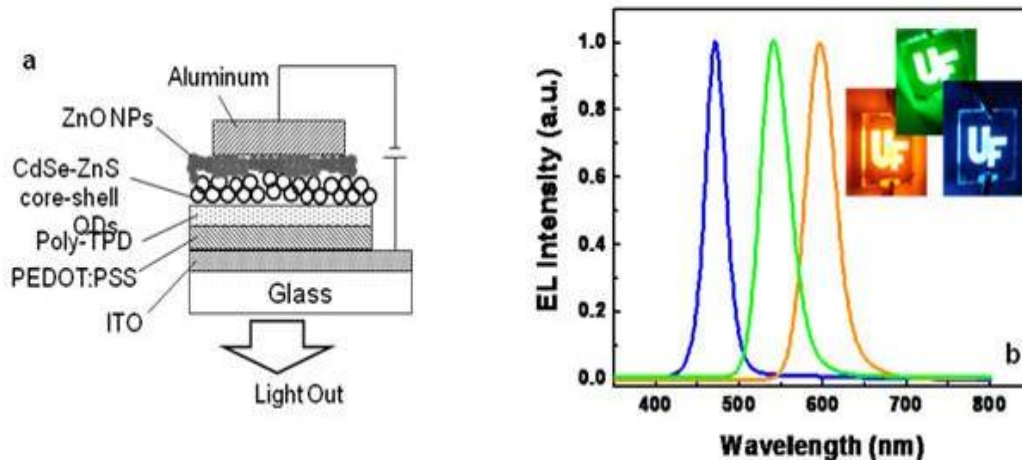


Fig. 6 (a) shows the device structure of the quantum LED and (b) shows the spectra of the RGB devices.

Lithium Ion Batteries

In order to improve the rate capability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The Li diffusion activation barriers of $\text{LiM}_{1/2}\text{Mn}_{3/2}\text{O}_4$ ($M = \text{Ti, V, Cr, Fe, Co, Ni}$ and Cu) are calculated by first principles computation. The results suggest that doping with Co or Cu can potentially lower Li diffusion barrier compared with Ni doping. $\text{LiNi}_x\text{Cu}_y\text{Mn}_{2-x-y}\text{O}_4$ were synthesized by sol-gel method. Although the capacity of the doped spinel materials decreases with the increasing doped Cu amount, $\text{LiCu}_{0.25}\text{Ni}_{0.25}\text{Mn}_{1.5}\text{O}_4$ spinel oxide exhibits higher capacity than undoped $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel at high rates (more than 2C). Among the three samples, D_{Li} of $\text{LiCu}_{0.25}\text{Ni}_{0.25}\text{Mn}_{1.5}\text{O}_4$ is one order of magnitude higher than that of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiNi}_{0.45}\text{Mn}_{1.55}\text{O}_4$ as shown in Figure 1. Moreover, a new explanation of the voltage profile for $\text{LiNi}_x\text{Cu}_y\text{Mn}_{2-x-y}\text{O}_4$ is proposed, supported by the results from first principles computation, and confirmed by electrochemical property measurement and *in situ* XAS experiment. We have shown that Cu cannot be further oxidized to Cu^{4+} and the plateau at 4.95V originates from extra electrons provided by oxygen ions.

Titanium dioxide flake nanostructures were fabricated by a simple spreading method. The pentane and titanium n-butoxide were used as the precursors and continuously added into the solution on the surface of flowing water. Their crystal structure, surface area, pore size and electrochemical properties are compared for flakes and nanoparticles. The electrochemical and structure properties of the nanoflakes are significantly influenced by subsequent heat treatment process. The calcined titanium dioxide flakes exhibits larger reversible discharge capacity, better rate capability and excellent cycling stability compared to Anatase titanium dioxide nanoparticles, due to their small grain size (8nm), larger surface area (7 times greater than particles) and porous structure (7nm). The smaller grain size of the flakes suggests the new LiTiO_2 forming during the lithiation process that improves the discharge capacity. The larger surface area of the flakes contribute to the larger electrode/electrolyte contact area, the short path lengths for both Li-ion and electron transport and lower specific current density of the active materials that lead to the better rate capability. The cycling performance of calcined flakes was benefited by its porous structure. At the same time, the nanosized grain (8nm) also excluded the extra strain formed during the lithiated process, which improves the cycling performance.

All-solid-state thin film batteries are most ideal sample for probing the intrinsic properties by Transmission electron microscopy (TEM), Scanning Probe Microscopy (SPM), X-ray Photoelectron Spectroscopy (XPS) and potentiostatic intermittent titration technique (PITT). A Lambda Physik KrF Excimer laser with wavelength 248nm was used for the thin film deposition. All-Solid-State thin film battery $\text{TiO}_2/\text{LVSO}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{stainless steel}$ was fabricated successfully. It is very difficult to investigate the surface film of the cathode electrode with composite form, especially when the fluorine peak of PVDF and carbon peak of carbon black are presented and overlap with real surface film. The solid electrolyte interface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ thin film without adding carbon black and PVDF was investigated by XPS. The result confirms that the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode material is a promising high voltage (5V) cathode material.

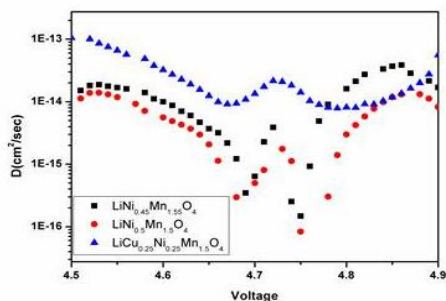


Fig. 7. Diffusion Coefficients of $\text{LiNi}_{0.45}\text{Mn}_{1.55}\text{O}_4$, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiNi}_{0.25}\text{Cu}_{0.25}\text{Mn}_{1.5}\text{O}_4$ (published in Chemistry of Materials, 2011, 23 (11) 2832)

For new cathode materials family - Li excess oxides, our research is designed to explore the effects of synthesis on the electrochemical properties of the material. We identified that the synthesis technique can alter the electrochemical performance of the material. Specifically we found that the surface characteristics as well as particle shape and distribution dramatically affect the electrochemical properties including cycling stability, rate capability and the lithium diffusion coefficient. This work is published in the Journal of the Electrochemical Society (2010). Once the complexity of interface in this material system was initially understood, the research progressed to identify the structural interface changes following electrochemical cycling. The characterization techniques linked the analysis of the electrolyte, the surface and the bulk of the cathode to gain a complete understanding of the delithiation mechanism. This research was performed through collaborations with the SHaRE program at Oak Ridge National Laboratory using their atomic-resolution TEM microscope and with Argonne National Laboratory with their synchrotron X-ray diffraction at the Advanced Photon Source (APS). The surface analysis led to the discovery of a new surface phase that is only 1 to 5 nm thick, which supports our previous research as well as led to the first detailed characterization of such a surface phase. This research provided a detailed cation rearrangement process and consequent phase transformation that can contribute to the variation of electrochemical properties following the charging/discharging cycle. More importantly such knowledge is pivotal to the optimization of these high voltage cathode materials. This work was published in Energy and Environmental Science, Figure 8 clearly depicts the existence of a surface second phase after electrochemical cycling.

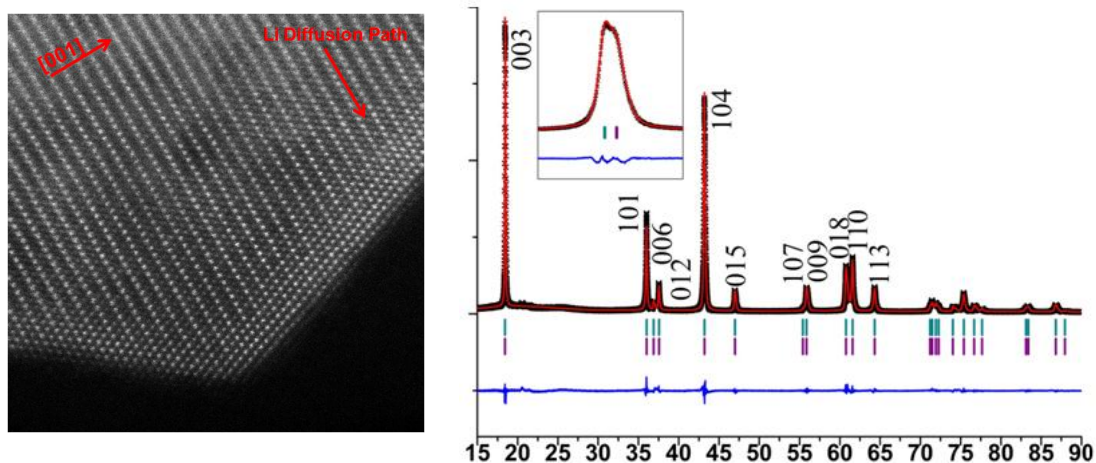


Fig. 8: Left: Atomic resolution STEM image of the material after electrochemical cycling. The diffusion path of Li is blocked by the presence of the heavy transition metal ions. Right: Synchrotron XRD refinement confirms the observation. This work is published in Energy and Environmental Sciences, 4, 2223-2233, 2011.

The analysis of structural changes before, during and following electrochemical property testing has led to a more thorough understanding of the Lithium transport mechanisms in the Li-excess series of materials. The findings from this research not only help to understand and eventually improve the Li-excess series of materials, but also can be expanded to other material systems to understand complex intricacies such as surface coatings, Li diffusion and oxygen loss mechanism, as well as phase transformation induced by ion migration. **The FESC student Chris Fell has been selected to receive the prestigious Electrochemical Society Battery Division Student Award.**