Cycling Effects on Lithium Vanadium Oxide Phosphate Rechargeable Battery Cathodes

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ABSTRACT

While the prevalence of reversible energy storage has grown in the past few decades, the need for longer-lasting batteries remains. Current batteries exhibit modest energy density capacities and degrade significantly over many cycles. This research focuses on a $LiVOPO_4$ compound as a battery cathode. Previous experiments have found this compound to exhibit an energy capacity between 250-270 mAh/g. This experiment involved the synthesis of $LiVOPO_4$ through ball milling and annealing (to achieve the desired P2 structure) and the creation of 12 half-cells. After assembling these cathodes into complete batteries in an argon-filled environment, an automatic cycler was used to charge and discharge these cells through a specified number of cycles. Then, removing these cells in their charged and discharged states after various numbers of cycles, these cathodes were extracted and structural changes were investigated using x-ray diffraction in the laboratory and x-ray absorption studies at the Advanced Photon Source (APS).

Figure 1. Glenbrook South group constructing batteries at IIT (Illinois Institute of Technology).

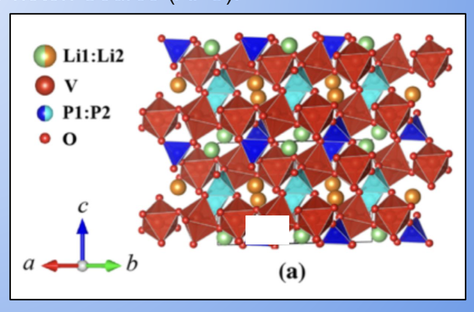

Figure 2. $LiVOPO_4$ P2 structure formed in experiment.

MOTIVATION

Figure 3. Glenbrook South team working with Dr. Segre (right) at the APS beamline.

While traditional rechargeable lithium-ion batteries have advanced to modest efficiencies, the exploration of cells with a $LiVOPO_4$ cathode could lead to further developments in rechargeable battery technology. Electric vehicles will surely benefit from the next generation of batteries that could withstand thousands of charging cycles and that can store a greater amount of energy when compared to that of current batteries. In addition, this experiment offers a wide range of learning opportunities for the students involved. Students actively participated in the research, design, manufacture, and test battery half-cells. The x-ray structural studies exposed students to large-scale equipment available at the Illinois Institute of Technology and the Argonne Advanced Photon Source as students understood how both large and small-scale structures can be studied using x-ray diffraction and x-ray absorption. Additionally, in conducting such an experiment, students work closely with professional scientist. Finally, the need to interact with primary resources in professional journals provided students with the opportunity to understand how scientific research is conducted today.

DATA COLLECTION & EXPERIMENTAL PROCESS

To synthesize Lithium Vanadium Oxide Phosphate, starting materials Li_2CO_3, NH_4VO_3, and $NH_4H_2PO_4$ were massed in a stoichiometric ratio of 1:1:1. The materials were combined through high-energy ball milling. This dry mixture was then compressed into pellets and annealed in an oven, heated in an argon atmosphere at 300°C for 5 hours to remove ammonia. The solid mixture was then heated for 10 hours in an argon atmosphere at 800°C. Through x-ray diffraction, the desired $LiVOPO_4$ crystal structure was observed. The pellets were then ball milled again into nano-sized particles. This active material (70%), carbon black (20%) or other conducting material, PVDF binder (10%), and NMP solvent (amount depended on viscosity) was combined to create a slurry that was then deposited onto a piece of aluminum foil, with a thickness of 80µm. After drying the slurry in an oven, quarter-sized pieces were cut from the foil and slurry sheet (Figure 4) and then assembled into battery cells in an argon-filled glove box (Figure 5). The batteries were constructed with the following materials layered in order as illustrated in Figure 6: cathode cap, spring, iron spacer, cathode material (LiVOPO4), 1M $LiPF_6$ electrolyte, polymer separator, anode material (lithium), and an anode cap.

A dozen half cells were created and tested by varying the charging voltage at 0.0V, 1.5V, 4.0V, 4.2V, and 4.5V. The electrodes were then removed from the battery for EXAFS analysis at the Argonne Advanced Photon Source (APS) for x-ray fluorescence studies to see see how the structure changed through the cycling process at different charging voltages (Figure 7).

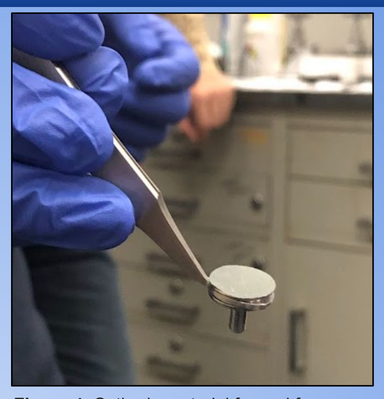

Figure 4. Cathode material formed from $LiVOPO_4$, the 'test material' in this battery.

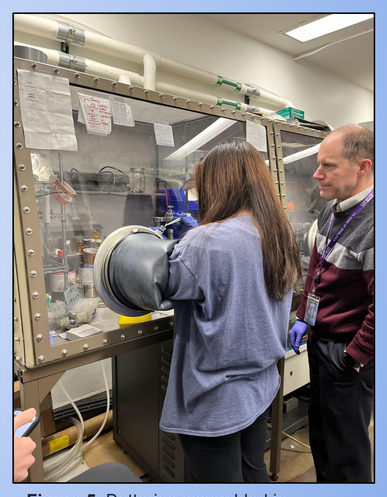

Figure 5. Batteries assembled in oxygen-free glovebox to prevent oxidation from occurring.

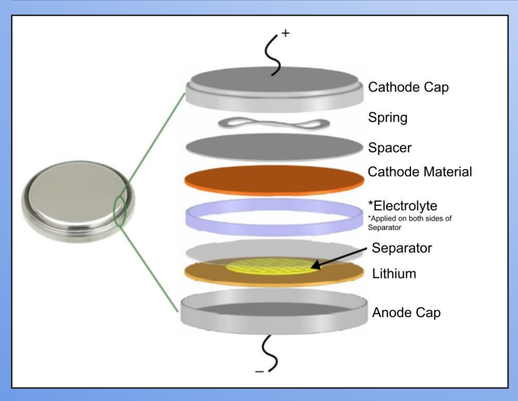

Figure 6. (Left) Diagram of coin cell battery components.

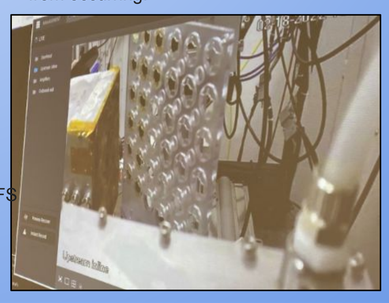

Figure 7. (Right) Array of cycled cathodes in EXAFS experimental station.

RESULTS

Cycling Data for $LiVOPO_4$ Cathode

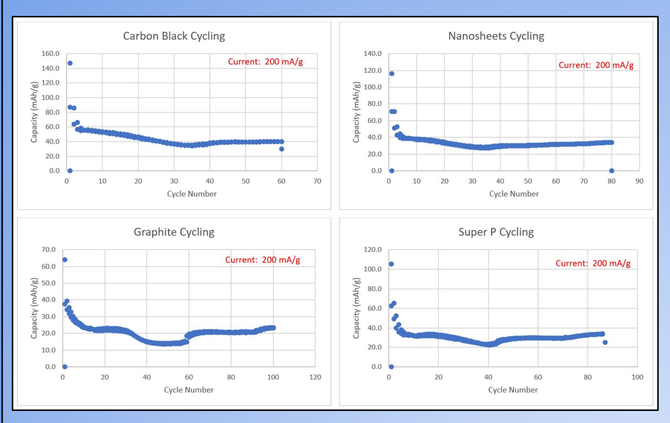

Figure 8. Four different conductive materials (20%) were used alongside the activity $LiPO_4$ material (70%) and PVDF binder (10%) to construct the battery cathode. The capacity was measured as a function of cycle number to determine if one particular conductive material is preferred over another. Carbon black yielded the greatest capacity when combined with our the active cathode material. Nonetheless, it can be seen that for all conductive materials, their capacities stayed relatively constant throughout many cycles.

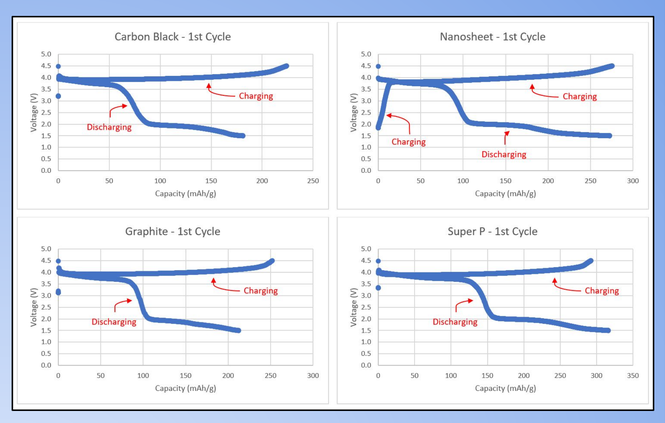

Figure 9. Capacity comparisons for four different conductive materials that were used alongside the $LiVOPO_4$ active material and the PVDF binder in the battery cathode construction. Each conductive material appears to behave similarly in voltage vs. capacity plots for the the first cycle charging and discharging. The relationship occurs when full charge cut-off voltage is achieved; the charging voltage begins to decline, first suddenly and then gradually.

Extended X-ray Absorption Fine Structure (EXAFS) Data for $LiVOPO_4$ Cathode

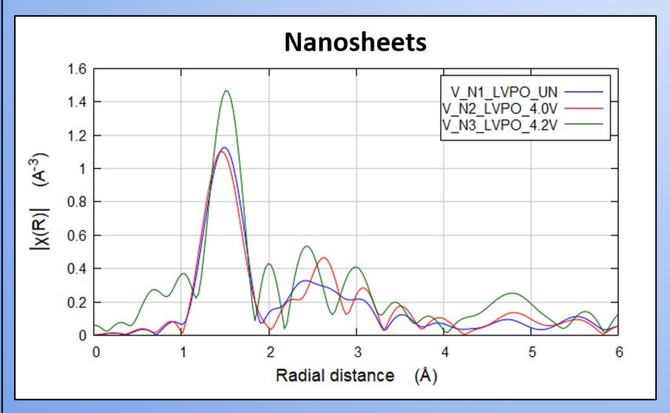

Figure 10. EXAFS plot for three different samples–uncharged, charged to 4.0 V, and charged to 4.2 V–using the nanosheets conductive material alongside the active cathode material. When measuring the EXAFS for the materials, data was unable to be captured for carbon black and graphite. As the voltage was increased for the nanosheet material, the radial distance between the atoms in the LVPO structure decreased.

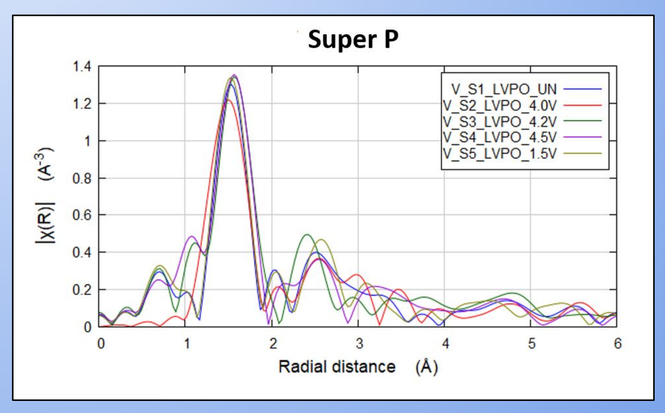

Figure 11. EXAFS plot for five different samples–uncharged, charged to 4.0V, charged to 4.2V, charged to 4.5V, and charged to 1.5V–using the Super P conductive material alongside the active cathode material. As the voltage was increased for the Super P material, it can be seen that the radial distance between the atoms increased. This result is interesting as it contrasts with the EXAFS data from the nanosheets material where radial distance decreased.

CONCLUSION

The material $LiVOPO_4$ combined with the four conductive materials–carbon black, nanosheets, graphite, and Super P–were first cycled and then analyzed at IIT to measure their voltages through the first charging and discharging cycle. After the first cycle, the batteries demonstrated only a modest drop in discharge capacity as a function of cycle. Through multiple cycles, the conductive materials each sustained a relatively constant capacity. This result is indicative that the material $LiVOPO_4$ functioning as a strong cathode candidate in a battery. At the APS, changes in the cathode structures through varying cycling voltages were observed. As voltage increased, the nanosheets' EXAFS data showed that the radial distance between neighboring atoms in the LVPO structure decreased, while the distance increased for Super P.

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