DREXEL UNIVERSITY
Materials Science and Engineering
College of Engineering

**Department of Materials Science and Engineering,**
**PhD Defense**

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**Hill Conference Room, Lebow Engineering**

# Synthesis Approaches for Novel Layered Cathode Materials for Li-ion and Beyond Li-ion Batteries

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Beyond-Li (BLI) ion-based batteries are rising in interest among researchers because of their utilization of more abundant, cost-effective charge carriers, including $Na^+$ and $K^+$ ions, compared to traditionally used $Li^+$ ions. However, because such systems utilize electrochemically cycling ions with larger ionic radii, achieving fast diffusion and high insertion rates of the BLI carriers into traditional, close-packed electrode materials is challenging. As such, these new systems require the development of novel electrode materials with high capacity, rapid charge transfer, and stable behavior over extended cycling. Materials with open, layered crystal structures have proven themselves among the most reliable electrode materials for Na-ion and K-ion based systems, exhibiting high performance in these emerging systems. Tuning and control of interlayer spacing and chemical composition in open layered structures, can be accomplished via simple wet chemical modification approaches. Such tailoring has the capability to increase ion movement and insertion as well as electrochemical stability, which may lead to improvements in electrochemical performance of these electrode structures.

Bilayered vanadium pentoxide ($\delta$-$M_xV_2O_5$) is a promising cathode material for BLI systems as vanadium can be present in its highest oxidation state, 5+, and can undergo multiple reductions to a 3+ state, allowing for the transfer of up to two electrons per vanadium ion. The bilayered structure is built from double layers of $VO_x$ polyhedra which are separated by a large interlayer spacing. The $\delta$-$V_2O_5$ phase exhibits an interlayer spacing of 11.5 Å which is stabilized by intercalated water molecules. While this structure exhibits high initial capacities, performance typically decays over extended cycling, due to lattice breathing and the gradual breakdown of the lamellar stacking of the V-O layers.

This dissertation focuses on the chemical pre-intercalation approach as a means to improve electrochemical performance of bilayered vanadium oxide electrodes in Na- and K-ion systems. Electrochemical performance of $\delta$-$M_xV_2O_5$ (M = Li, Na, K, Mg, Ca) in Li-ion cells will also be presented as a reference. This chemical pre-intercalation technique will be demonstrated to improve electrochemical performance through three modes: (1) pre-intercalation of charge-carrying into the bilayered phase can lead to tailored ion transport and increase overall specific capacities, (2) optimization of interlayer water content, improvement of structural order, and increase of intralayer bonding to improve electrochemical stability, and (3) pre-intercalation of electrochemically inactive organic and inorganic ions in order to stabilize the bilayered structure and improve capacity retention through BLI ion cycling. A detailed study of the mechanism of charge storage and the effect of charge-carrying ion size on demonstrated capacities and electrochemical stability in Li-ion, Na-ion and K-ion batteries will also be discussed. A methodology to improve electrochemical performance via chemical pre-intercalation is investigated.