

Nanostructured Layered Cathode for Mg-ion Batteries

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Introduction Rechargeable battery systems with different transporting ions that can provide an alternative choice to Li batteries would bring substantial relief and expansion of the existing energy storage market. To achieve substantially greater energy density than Li-ion magnesium batteries are the most promising technology. Furthermore, because of its “green” character Mg is environmentally friendly, with high natural abundance in the Earth’s crust (13.9% as compared to 0.0007 % for Li), and atmospheric stability. Due to the divalent nature of Mg ions and the use of a magnesium metal anode, magnesium batteries can obtain higher energy density than state-of-the-art lithium batteries. However, magnesium electrochemistry suffers from serious limitations due to anode/electrolyte incompatibility. Using pure Mg as anode/counter electrode in electrochemical magnesium deposition/dissolution reaction is known to be hazardous for practical use. Alternative material families, as well as new design approaches, are highly desirable for ultimate industrialization of Mg secondary batteries¹.

Results and Discussion Exploration for new cathode materials for rechargeable Mg batteries is focused on intercalation compounds exhibiting a higher working potential and capacity. Due to the divalence of Mg²⁺ ions, it is generally foreseen that the intercalation of Mg²⁺ ions is somewhat difficult and complex². When transporting ions have much larger diameter or charge than the host metal ion, segregation of transporting and host metal ions in the crystalline structure is inevitable. In this case deintercalation will lead to the collapse of the crystalline structure and breaking of electric conductance. Therefore, in the case of Mg²⁺ ions, only layered structures with large layer spacing are able to support reversible cycling. Furthermore, layered materials have potential to control polarizability of Mg²⁺ ions by adjusting layer spacing. Nanostructured bilayered V₂O₅ is highly efficient 3 V cathode material for ambient temperature sodium ion batteries³. It shows superb performance: theoretical reversible capacity for Na₂V₂O₅ stoichiometry of 250 mAh/g, excellent rate capability and cycle life, as well as high energy and power densities. My preliminary results show that it is possible to extend the reversible ion-insertion chemistry of nanostructured layered V₂O₅ beyond lithium and larger in size Na⁺ ions to those with higher charge: Mg²⁺ ions (**Figure 1**). Electrochemical synthesis is a method of choice for preparation of nanoscale architectures that require excellent electronic conductivity. It eliminates the need for conductive carbon additives and binders typically used in conventional electrodes that alter their long-term stability. In order to increase V₂O₅ loadings to be suitable for practical applications, we developed in situ growth of the V₂O₅ nanoribbons on highly conductive, interconnected substrate: carbon nanofoam (CNF). Mg-ion full cell was constructed from bilayered V₂O₅/CNF cathode and CNF

anode in 1M Mg(ClO₄)₂/PC. We replaced Mg metal anode as a source of Mg ions with electrochemically discharged (Mg-ion rich) nanostructured V₂O₅ cathode (**Figure 1**, Discharged V₂O₅ from Mg-ion half cell). In our preliminary results in electrolytes based on propylene carbonate these electrode materials were able to retain the local electro-neutrality rapidly upon accepting Mg²⁺ ions and were able to reversibly intercalate Mg ions over prolonged cycling.

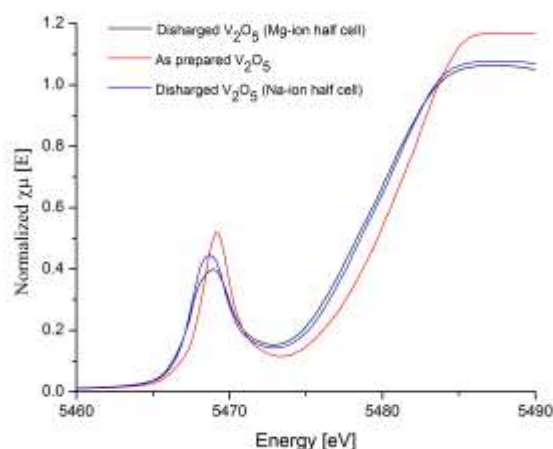


Figure 1. Normalized V K-edge XANES for as prepared, bilayered V₂O₅ (V⁵⁺ standard) compared to discharged V₂O₅ in Na-ion half-cell (V⁴⁺ standard) and discharged V₂O₅ in Mg-ion half-cell.

Conclusions We have developed safe, Mg-ion battery systems exclusively made by nanoelectrodes emphasizing the importance of tailoring nanoarchitecture of electrode materials and opening up new opportunities for rechargeable Mg batteries.

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