

Exploring New Cathode Materials to Enable High Energy Magnesium Batteries

Elyssa Ferguson, B.S.¹ and Janna Eaves-Rathert, B.S.²

¹University of Maryland, Baltimore County, efergus1@umbc.edu

²Vanderbilt University, janna.m.eaves.1@vanderbilt.edu

Abstract – Modern smartphones, electric vehicles, drones, and other evolving technologies demand improvement of Li-ion batteries into more energy-dense power sources. Magnesium (Mg) batteries are a promising alternative because the Mg^{2+} ion shuttles twice as many electrons as Li^+ , thereby doubling the theoretical volumetric energy density. Here, we investigate the storage capacity and Mg-ion hosting mechanisms of tungsten diselenide (WSe_2) as a cathode material for these cutting-edge battery systems. Using a three-electrode electrochemical setup, we measured a high specific capacity of 120 mAh/g and subsequently characterized the material at 0%, 50%, 75%, and 100% discharge via X-ray diffraction and Raman. Characterization showed no indications of Mg- WSe_2 conversion reactions, and the amount of intercalation of Mg^{2+} into WSe_2 remains uncertain. Further experimentation with more compatible electrolytes is necessary to confirm hosting mechanisms of WSe_2 . This work opens a door to energy-dense multivalent ion batteries that surpass current lithium-ion technologies in cost, safety, and size.

Keywords – Tungsten Diselenide Cathode, Magnesium-Ion Battery, Multivalent Batteries

I. INTRODUCTION

A myriad of technologies depends on portable energy storage technology, such as lithium-ion (Li-ion) batteries to function. Personal devices like smartphones require battery storage, yet, the demand for energy storage technology will only continue to increase as more products, including electric vehicles, drones, and renewable energy sources, demand batteries for portable energy storage. Li-ion batteries are largely used to store energy in small and large-scale systems. Despite technological improvement of the Li battery, there still exist limitations in energy capacity due to lower power density [1]. Likewise, safety hazards of the Li-ion battery due to dendrite formation and heat generation, as well as a limited availability of the natural resource and high production costs pose additional hurdles [1, 2]. To meet the increasing demand for more powerful, lighter, and affordable energy storage devices, magnesium (Mg) is a potential alternative to the Li-ion batteries [3].

Multivalent batteries present opportunities for future development of higher capacity energy storage devices. Specifically, Mg-ion batteries are potential candidates to

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overcome technological hurdles that currently bottleneck further development of Li-ion batteries. Within a discharging electrochemical cell, electrons travel through the device requiring power, while ions simultaneously move from the anode into the cathode. This process occurs to operate battery-powered devices. For example, a lightbulb, seen below in Fig. 1, illuminates a room when electrons (e^-) pass through a lightbulb via an external path, while ions, illustrated as Mg ions (Mg^{2+}), move between the electrodes, the anode and cathode, by means of electrolyte inside the cell.

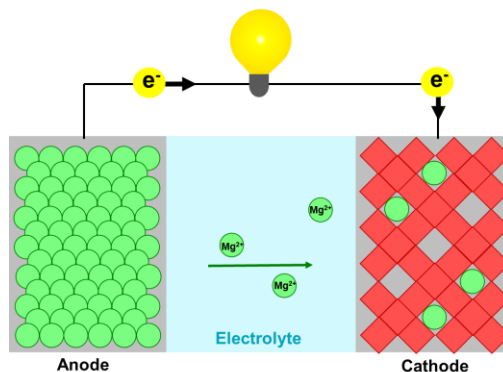


Fig. 1 Mg ions traveling from the anode to cathode during the discharge state

Mg is a promising alternative because the Mg^{2+} ion shuttles twice as many electrons as Li^+ between the anode and cathode of a battery due to its divalent nature, providing twice as much energy in an electrochemical cell.

In fact, Mg's theoretical volumetric energy density is almost double that of lithium [4]. Additionally, Mg batteries should be more affordable for consumers and less costly to produce because Mg (1.94%) is more abundant than Li (0.006%) in the earth's crust [1, 5, 6]. The prospect of more energy dense, affordable batteries is potentially viable with Mg.

Mg demonstrates promise as an alternative for Li-ion batteries, yet much information regarding the chemistry of electrodes compatible in Mg-ion electrochemical cells remains unknown. Specifically, the discovery of high capacity, high voltage cathodes is necessary for the development of next generation storage devices. Higher capacity cathodes store a higher quantity of ions per unit mass and consequently increase the battery's overall capacity.

Cathode materials, such as titanium diselenide ($TiSe_2$) and titanium disulfide (TiS_2), have been explored and yielded promising results [4, 7, 8]. Yet, little is known about tungsten

diselenide (WSe_2), a chalcogenide composed of a layered structure that could host Mg ions (Fig. 2) [1, 4, 9]. WSe_2 has a higher theoretical volumetric energy density (1578 Wh/l) than TiSe_2 (566 Wh/l) and layered TiS_2 (623 Wh/l) [4], but existing studies of WSe_2 used electrolytes that approached or exceeded the electrochemical stability windows of the system and did not provide sufficient structural characterization to support their results [1, 9]. Here, we thoroughly investigate the Mg-ion hosting mechanisms of WSe_2 and attempt to determine the true storage capacity of this cathode material.

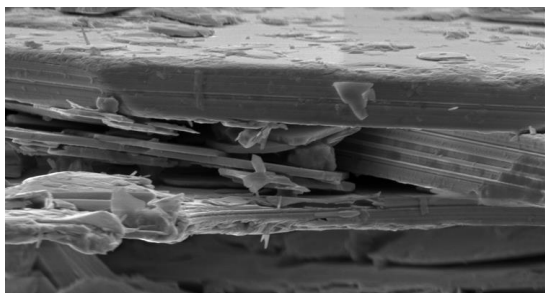


Fig. 2 SEM image of WSe_2 layers

II. EXPERIMENT RESULTS & DISCUSSION

To test the ion storage capability of WSe_2 , we constructed a three-electrode electrochemical setup. The working electrode, WSe_2 on platinum; the pseudo-reference electrode, activated carbon on platinum; and the counter electrode, platinum foil, were immersed in an electrolyte solution composed of magnesium perchlorate in acetonitrile. The pseudo-reference electrode potential was calibrated to be 3.22 V vs Mg/Mg^{2+} . With the three-electrode electrochemical setup, we observed quasi-reversible reactions at 1, 5, 10, and 20 mV/s scan rates, where the voltage ranged from -1.5 V to 0.5 V vs activated Mg/Mg^{2+} . Using galvanostatic methods at a C/10 rate, we measured the specific capacity of WSe_2 to be 120 mAh/g. Next, we characterized the WSe_2 materials at 0%, 50%, 75%, and 100% discharge (Fig. 4) via X-ray diffraction (Fig. 5a, 5b) and Raman (Fig. 5c) to gain a better understanding of the Mg-ion hosting mechanisms. Mg ions were believed to insert themselves within the layers of WSe_2 during discharge.

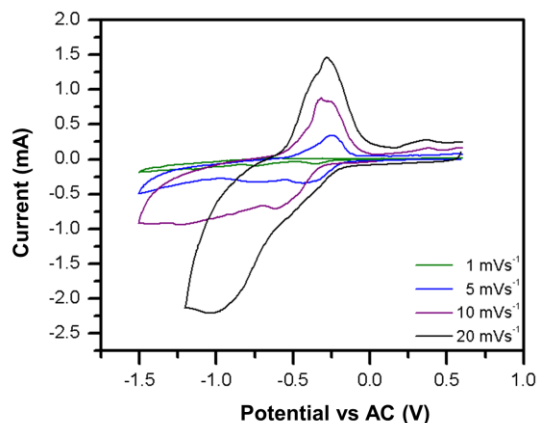


Fig. 3 Voltammograms at 1, 5, 10, and 20 mV/s scan rates

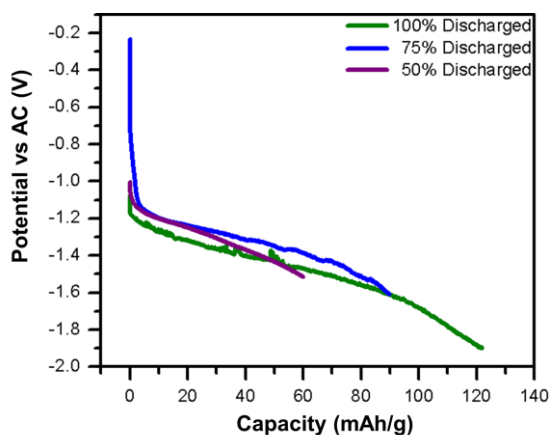


Fig. 4 Curves at 100%, 75%, and 50% discharge states

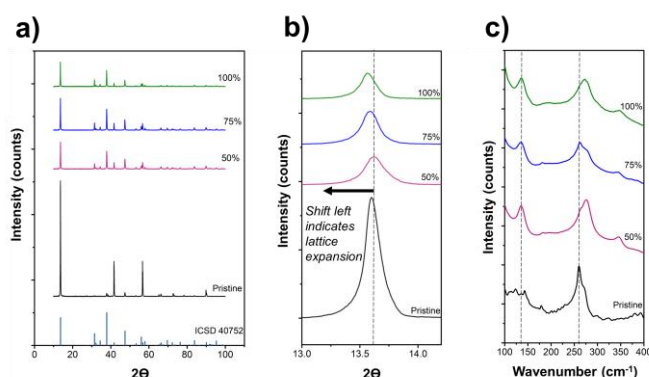


Fig. 5 (a,b) XRD patterns (c) Raman spectrum spectra of WSe_2 discharging for 5, 7.5, and 10 hours

X-ray diffraction (XRD) patterns of 50%, 75%, and 100% discharge states demonstrated peak shifts to the left in Fig. 5b. As governed by Bragg's Law, this shift to the left indicated the WSe_2 lattice was expanding; however, the peak shift was much smaller than expected for accommodation of 120 mAh/g capacity. Raman tests of 50%, 75%, and 100% discharge states provided additional information suggesting the intercalation of Mg ions. In Raman spectra in Fig. 5c, a peak at the 250 cm^{-1} wavelength shifted to a higher wavelength at 50% discharge, then returned to the 250 cm^{-1} wavelength at 75% discharge, only to increase again in wavelength at 100% discharge. These changes in wavelength are indicative of the bonds stretching and relaxing, similar to the expansion and compression of a spring. Although there was no observed change in crystal structure or bonding arrangement that would suggest a conversion reaction, the amount of intercalation of Mg into WSe_2 remains uncertain. As such, the observed charge storage in electrochemical data may be largely attributed to side reactions at the surface or interface of WSe_2 . In the future, it will be important to repeat these experiments using advanced electrolyte formulations that are developed to support study of high-voltage cathode materials.

III. CONCLUSION

Multivalent batteries are potentially feasible alternatives to present-day Li-ion energy storage devices. While Mg-ion batteries are a promising option, work must be done to ensure that the materials comprising the cathode, anode, and electrolyte within an electrochemical cell are well-matched. We initiated an investigation of WSe_2 's storage capacity and its Mg-ion hosting mechanisms to understand the performance of the cathode material for Mg-ion battery applications. Our findings show that WSe_2 is prone to side reactions, and amount of intercalation of Mg into WSe_2 is yet to be determined. Further studies are required to study the types of chemical reactions and to identify multivalent electrolyte systems compatible with the layered chalcogenide [10]. With additional measured performance, there is great potential for energy dense multivalent ion batteries that surpass current Li-ion technologies.

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