



# Dual effect of structure and hydration on magnesium-ion insertion into electrodeposited $V_2O_5$ thin films

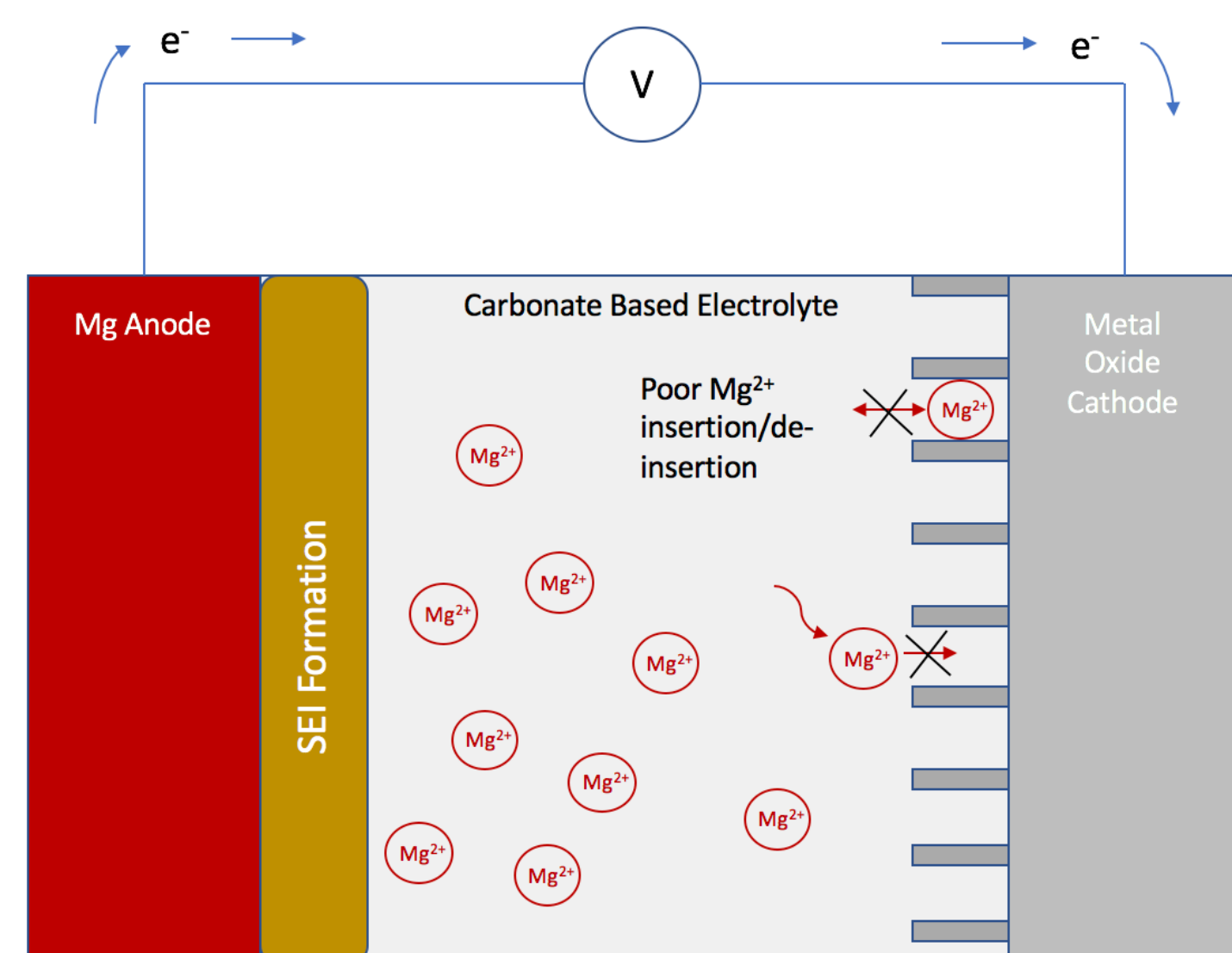
Brandon Johnston\*, Hakeem Henry\*, Emily Sahadeo\*, Darrin Liao\*, and Sang Bok Lee\*

\*Department of Chemistry and Biochemistry  
University of Maryland, College Park, MD



## Introduction

As global energy needs increase, there is a growing demand for safe, cheap, and powerful energy storage materials. Lithium ion batteries, the current state of the art in battery technology, are beginning to reach their limits in terms of the amount of energy density they can offer. Magnesium-ion batteries show promise as potential candidates to fill this demand as a result of their large energy density and specific volumetric capacity. When compared with conventional ion battery technologies, such as lithium-ion batteries, the raw materials for magnesium ion batteries are more abundant, and they are much safer. However, a few significant challenges have slowed progress in magnesium ion battery research; such as poor magnesium-ion insertion reversibility at the cathode interface, passivation at the anode surface, and poor compatibility with electrolyte solvents<sup>1</sup>.

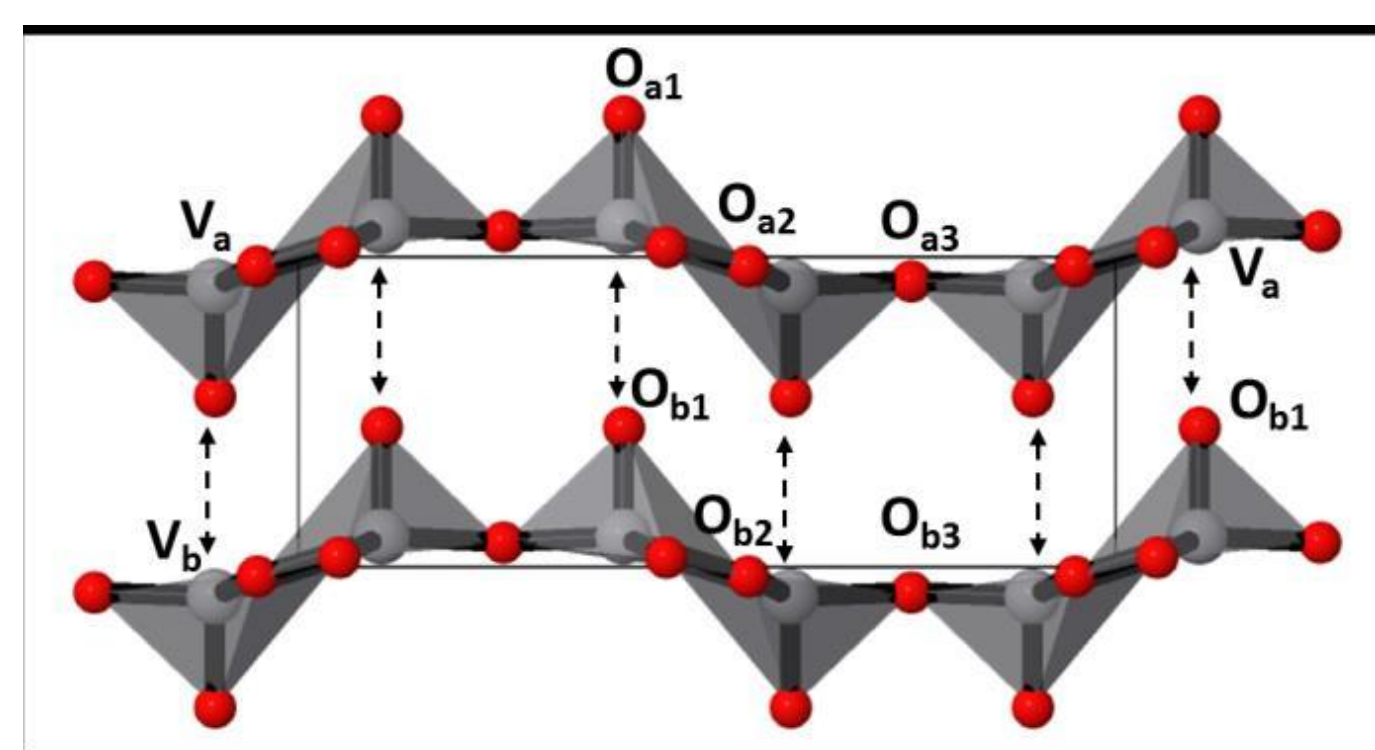


Schematic of Standard Mg-ion battery

## Cathodes

Mg batteries suffer from slow reaction kinetics at the cathode interface due to strong electrostatic repulsion attributable to the bivalence of the Mg ion. As a result, we chose to focus on improving Mg-ion insertion/de-insertion kinetics by enhancing the performance of  $V_2O_5$ , a well studied metal oxide redox active material for Mg ion batteries.

Vanadium (V) Oxide is a popular cathode material candidate for magnesium-ion batteries owing to its high stability, operating voltage, and specific capacity in its crystal form<sup>1</sup>. However, new research suggests that amorphous  $V_2O_5$  cathodes might offer greater capacity for Mg-ion insertion owing to their larger interlayer spacing. In this work, we evaluate this claim by comparing the electrochemical performances of increasingly crystalline electrodeposited  $V_2O_5$  thin films.

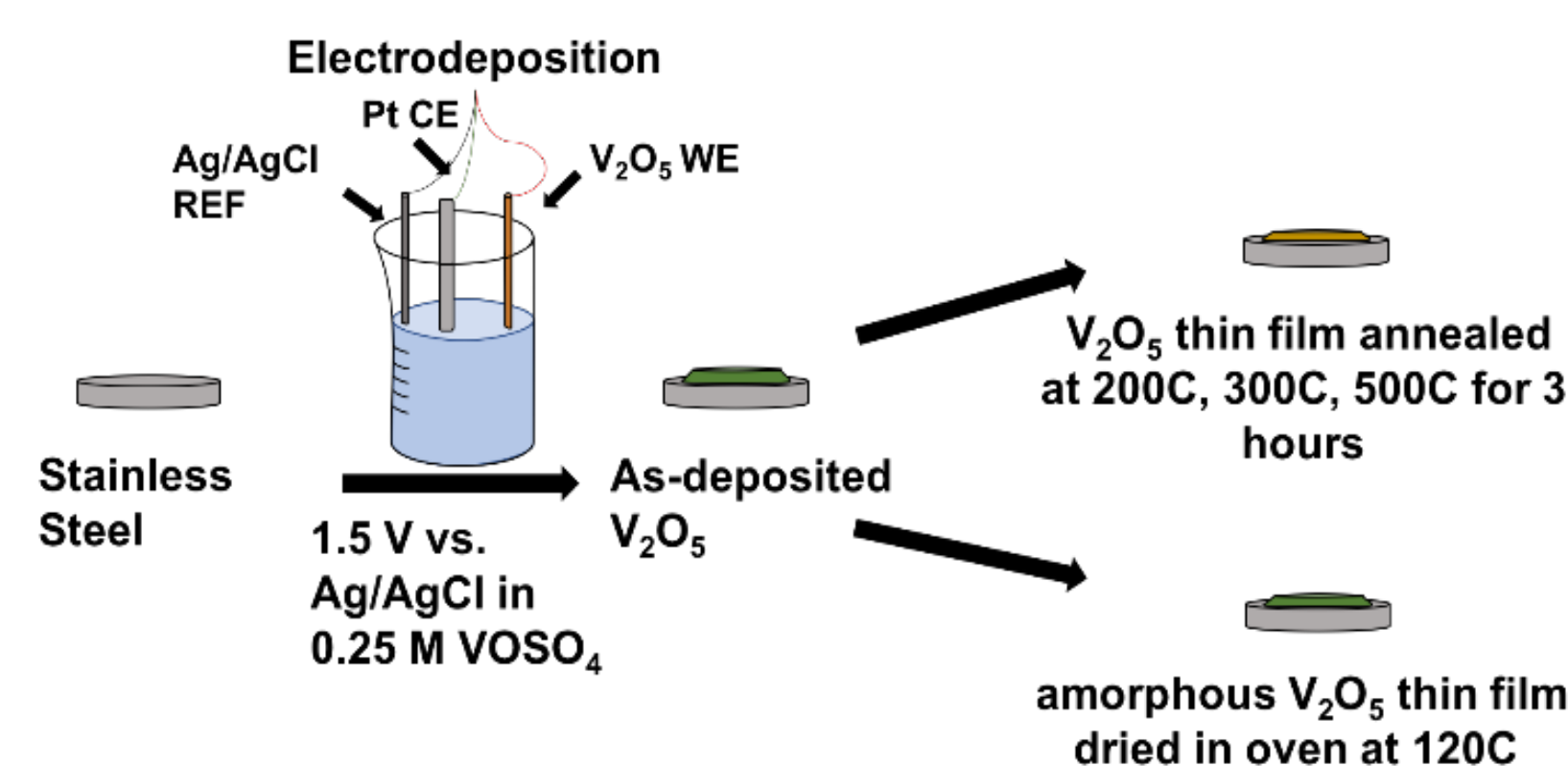


Crystal lattice structure of  $V_2O_5$

## Cathode Development

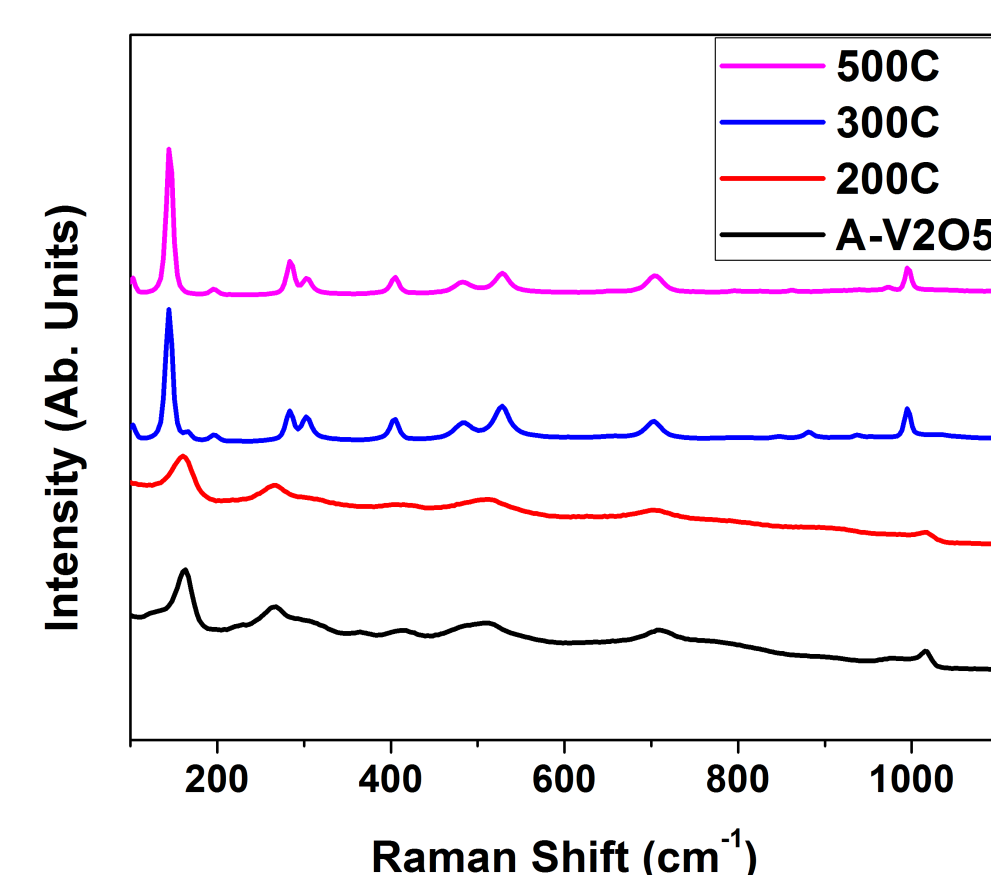
### $V_2O_5$ Thin Film Formation

$V_2O_5$  was used as the high capacity redox-active material for Mg-ion storage. Thin film cathodes were synthesized potentiostatically using a stainless steel spacer template. By holding a constant voltage of 1.5 V vs. Ag/AgCl in a solution containing 0.25 M vanadyl sulfate,  $V_2O_5$  was deposited onto the surface of the stainless steel. Samples were then annealed in air at 200, 300, or 500C for 3 hours. Amorphous samples were not annealed.

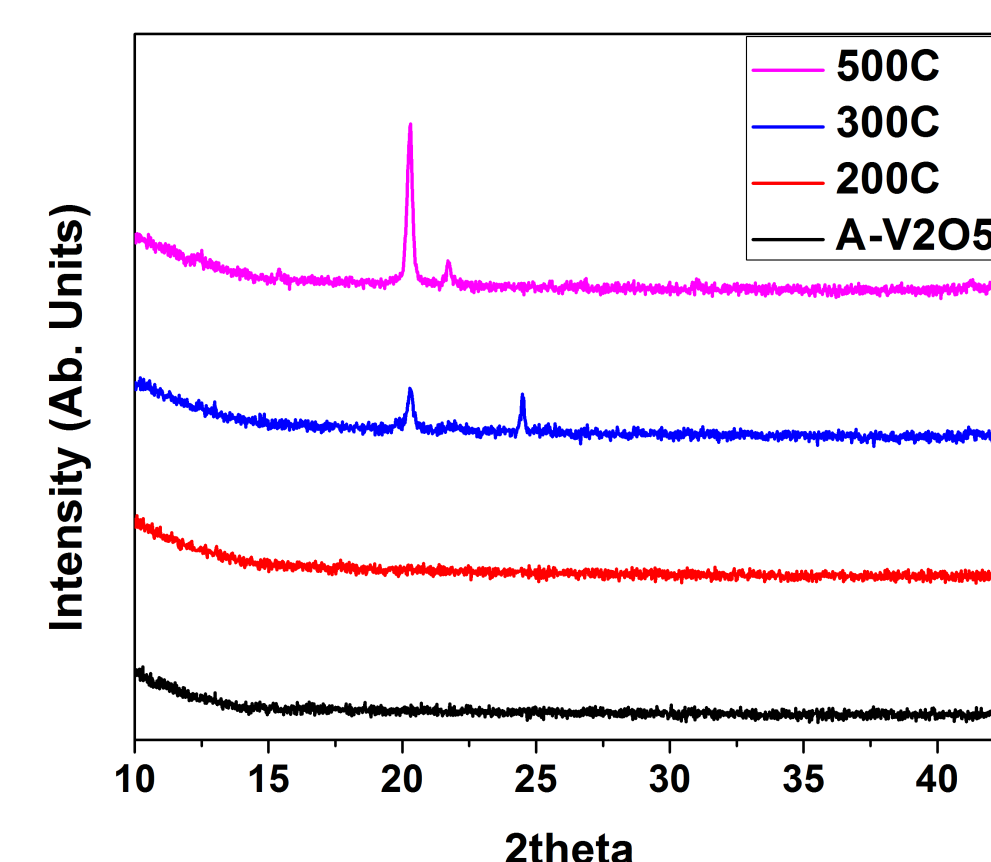


Schematic of the electrodeposition and annealing of the  $V_2O_5$  films.

### Characterization of Crystallinity



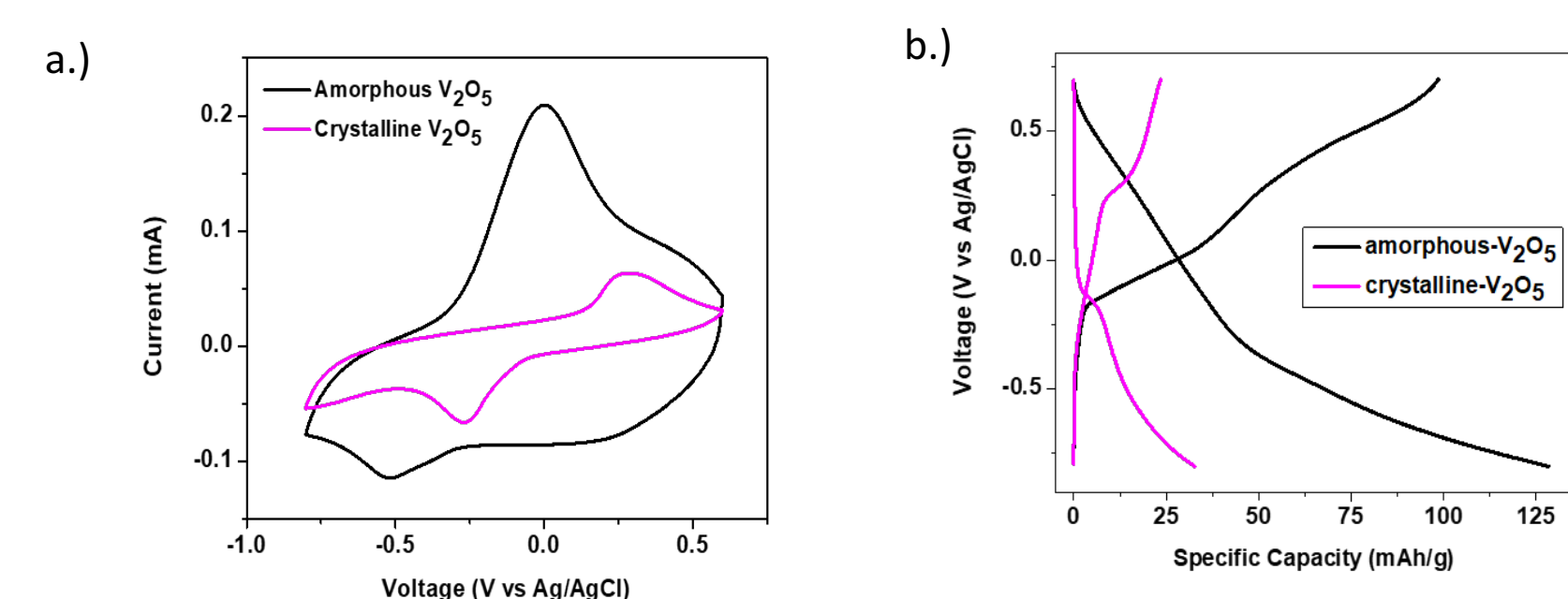
Raman spectroscopy data for  $V_2O_5$  thin films annealed at increasing temperature. A clear transition to long-range crystalline  $V_2O_5$  can be seen when samples are annealed at temperatures greater than 300C. A-V2O5 stands for amorphous  $V_2O_5$ .



XRD data for  $V_2O_5$  thin films annealed at increasing temperature. A clear transition to long-range crystalline  $V_2O_5$  can be seen when samples are annealed at temperatures greater than 300C by the emergence of peaks at 20°, 22°, and 24°. A-V2O5 stands for amorphous  $V_2O_5$ .

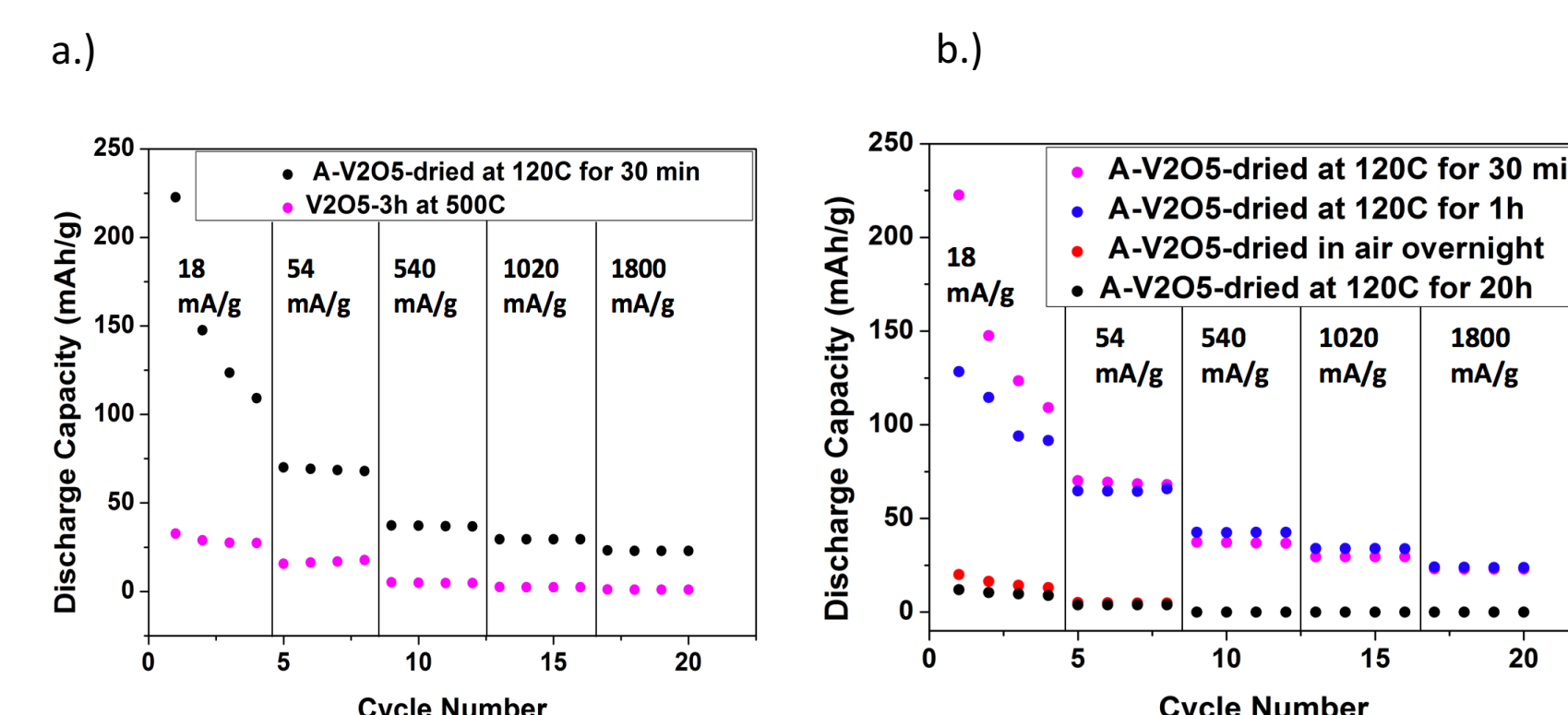
## Electrochemical Analysis

### CV and Charge-Discharge Cycling Performance

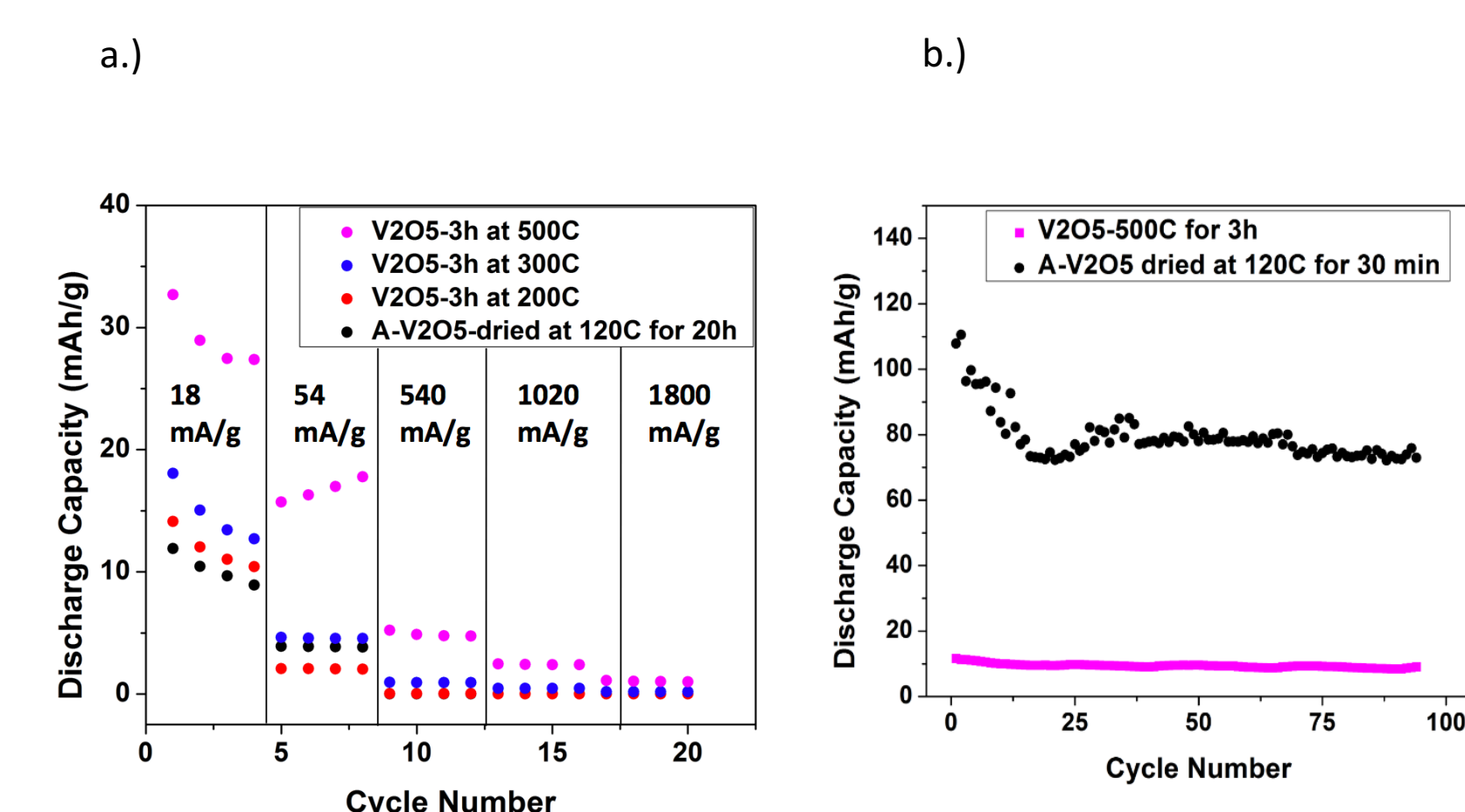


a.) Rate Performance Data for Amorphous and Crystalline  $V_2O_5$  (500C) cycled in 0.1 M  $Mg(ClO_4)_2 \cdot 6H_2O$ . Amorphous  $V_2O_5$  outperforms crystalline  $V_2O_5$  (500C) at every current density. b.) First cycle discharge and charge capacity for amorphous and 500C annealed  $V_2O_5$  at low current density. It should be noted that the amorphous  $V_2O_5$  samples did not go through a rigorous drying protocol.

### Rate Performance Data



a.) Rate Performance Data for Amorphous and Crystalline  $V_2O_5$  cycled in 0.1 M  $Mg(ClO_4)_2 \cdot 6H_2O$ . Amorphous  $V_2O_5$  outperforms crystalline  $V_2O_5$  at every current density. b.) Rate Performance Data for Amorphous  $V_2O_5$  samples with variable drying protocols. Increasing drying time results in lower capacity, which suggests that structural water content is crucial for mg-ion insertion into electrodeposited  $V_2O_5$  thin films.



a.) Comparison of rate performance of amorphous  $V_2O_5$  dried at 120C for 20 hours with annealed  $V_2O_5$  samples. All samples were cycled in 0.1 M  $Mg(ClO_4)_2 \cdot 6H_2O$ . b.) Long term cycling comparison between an amorphous  $V_2O_5$  thin film dried at 120C for 30 minutes and a  $V_2O_5$  thin film annealed at 500°C for 3 hours.

## Conclusion and Future Studies

In recent studies, there has been discrepancy as to whether amorphous or crystalline  $V_2O_5$  offers superior mg-ion storage capabilities. The aim of this work was to investigate both crystalline and amorphous  $V_2O_5$  structures in order to determine a link between crystallinity and electrochemical performance. As supported by the comparative rate performances of dry and wet amorphous samples, structural water is crucial for achieving high capacity magnesium-ion storage in electrodeposited  $V_2O_5$  thin films. We suspect that structural water enhances mg-ion insertion into  $V_2O_5$  for three reasons. Structural water may contribute to charge shielding of  $Mg^{2+}$  species, and increase void spacing for multivalent ion insertion. Additionally, increased water content may lead to higher capacity attributable to increased levels of proton insertion. At this point, we cannot conclusively report on the impact of structure, although it appears that there is no significant difference in the performance of dry amorphous and crystalline thin film samples. Thus, we postulate that, in the case of electrodeposited thin films, the advantage comes from the water that is integrated into the thin film structure during deposition. Although the role of water in promoting magnesium-ion insertion into  $V_2O_5$  is well studied, it must also be carefully considered when evaluating amorphous and crystalline  $V_2O_5$  structures prepared via aqueous deposition methods, as electrochemical performance will change significantly depending on the extent of structural hydration.

Future work will include ICP-MS analysis in order to quantify the amount of magnesium inserted into the  $V_2O_5$  thin films during cycling experiments. Furthermore, ICP-MS analysis will give an indication of how much of the capacity is attributable to proton insertion rather than magnesium insertion. In addition to ICP-MS, we will perform thermogravimetric analysis in order to more clearly relate drying protocols with water loss. This way, we will be able to distinguish the effects of loosely bound surface water and more tightly bound lattice water on thin film capacity. Lastly, in order to study the effect of  $V_2O_5$  crystallinity independent of structural water content, we would like to compare the electrochemical performance of amorphous and crystalline  $V_2O_5$  prepared from ultrahigh vacuum deposition processes, such as atomic layer deposition (ALD).

## References

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## Acknowledgements

