

# Study on the Electrochemically Stabilizing Effect of the High Dielectric Constant Oxide Artificial Solid Electrolyte Interphase on Electrodes in Aqueous Electrolytes

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Primary CNF Tools Used: Oxford ALD FlexAL

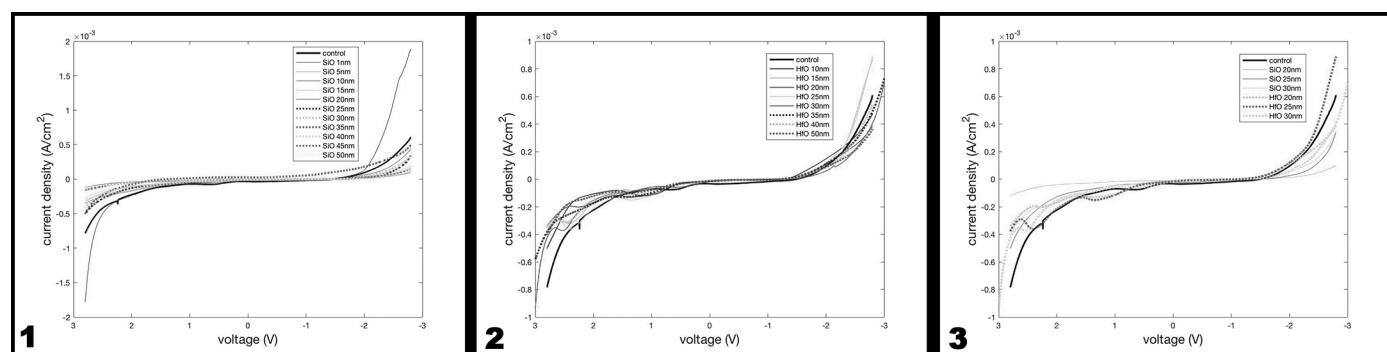
## Abstract:

Aqueous electrolytes, which have huge advantages in fire-hazard safety issues, are now still suffering from their narrow electrochemical stability windows. With the goal to study how ultra-thin oxide coatings can help to extend the stability windows of aqueous electrolytes, and more specifically, how band gap and dielectric constant affect the effectiveness of the oxide coatings, several high dielectric constant ( $k$ ) metal oxides with different thicknesses were coated onto polished stainless-steel squares. The coated stainless-steel squares were then used to test the stability of aqueous electrolyte in a symmetric cell setup with one molar of lithium sulfate using cyclic voltammetry. The results show that an ultra-thin high  $k$  oxide layer helps to increase the stability window of the 1M  $\text{Li}_2\text{SO}_4$  aqueous electrolyte to about five volts. However, no significant correlation between the width of the stability window and the dielectric constant or band gap of the coating materials was observed.

## Summary of Research:

Artificial ultra-thin metal oxide was coated onto 1 cm by 1 cm polished stainless-steel squares (brought from McMaster-Carr Supply Company) by atomic layer deposition (ALD) [1] using the Oxford ALD FlexAL at Cornell NanoScale Science and Technology Facility (CNF). It has been shown in previous research that an ultra-thin (usually around 15 nm) alumina coating

on electrodes can largely increase the electrochemical stability of a rechargeable battery [2]. Therefore, two other high dielectric constant ( $k$ ) metal oxides, silicon dioxide ( $\text{SiO}_2$ ) and hafnium dioxide ( $\text{HfO}_2$ ) [3], were applied at various thicknesses for studying. For each oxide coating, 1 nm, 5 nm, 10 nm, 15 nm, 20 nm, 25 nm, 30 nm, 35 nm, 45 nm, and 50 nm coatings were investigated. The cyclic



**Figure 1, left:** The cyclic voltammetry results for a typical symmetric  $\text{SiO}_2$  coated stainless steel electrode versus  $\text{SiO}_2$  coated stainless steel electrode cell with 1M aqueous lithium sulfate ( $\text{Li}_2\text{SO}_4$ ) at various coating thicknesses. **Figure 2, middle:** The cyclic voltammetry results for a typical symmetric  $\text{HfO}_2$  coated stainless steel electrode versus  $\text{HfO}_2$  coated stainless steel electrode cell with 1M aqueous lithium sulfate ( $\text{Li}_2\text{SO}_4$ ) at various coating thicknesses. **Figure 3, right:** A comparison between the cyclic voltammetry results for a symmetric  $\text{SiO}_2$  coated half-cell and a symmetric  $\text{HfO}_2$  coated half-cell with 1M aqueous lithium sulfate ( $\text{Li}_2\text{SO}_4$ ) at various coating thicknesses.

voltammetry results for a typical symmetric  $\text{SiO}_2$  coated stainless steel electrode versus  $\text{SiO}_2$  coated stainless steel electrode cell with 1M aqueous lithium sulfate ( $\text{Li}_2\text{SO}_4$ ) were summarized in Figure 1.

Figure 1 shows that, as the thickness of the  $\text{SiO}_2$  layer increases, the stability window of the coin cell is improved. At 20 nm thickness, where the best stability is achieved, the stability window is increased from 3V (baseline generated by the uncoated stainless-steel control cell) to about 5V, which is about 66.7% improvement. For thicknesses beyond 20 nm, no further significant improvement is observed.

Figure 2 contains the cyclic voltammetry for the same coin cell setup with  $\text{HfO}_2$  coating instead of  $\text{SiO}_2$ . Figure 2 proves that a thin layer of  $\text{HfO}_2$  can also improve the stability of such aqueous electrolyte system, especially in the positive potential region. Different from  $\text{SiO}_2$  coating,  $\text{HfO}_2$  coating gives the best stability window enhancement at thickness around 35 nm. For  $\text{HfO}_2$  coating that is thicker than 35 nm, no further significant improvement is observed.

Considering the results from both  $\text{SiO}_2$  and  $\text{HfO}_2$  coatings, it can be concluded that a semi-conducting or insulating protective layer can expand the stability window for an aqueous battery system. Initially, as the thickness of the coating increases, the stability window also increases. Until a certain thickness (25 nm for  $\text{SiO}_2$  and 35 nm  $\text{HfO}_2$ ), the stabilizing effect reaches its maximum and for thickness beyond this value, no further improvement can be achieved.

Figure 3 is a comparison between  $\text{SiO}_2$  and  $\text{HfO}_2$  coating. It shows that at the same thickness (which is thinner than 35 nm), the  $\text{SiO}_2$  coating gives a wider stability window

than the  $\text{HfO}_2$  coating does. Additionally, it is observed that there is a reaction peak around 2.2V for  $\text{HfO}_2$  coated symmetric half-cell systems, while such a peak cannot be found on the  $\text{SiO}_2$  coated symmetric half-cell system. This might indicate that the  $\text{HfO}_2$  coating reacts with water or aqueous  $\text{Li}_2\text{SO}_4$  solution at 2.2V, which suggests that  $\text{SiO}_2$  is a more stable coating material to be used in aqueous electrolyte system.

The SEM results of cycled coated electrodes provide evidence. After 11 cyclic sweeps, no  $\text{HfO}_2$  could be found at the surface of the electrodes, but  $\text{SiO}_2$  was still found evenly covering the entire surface. However, further investigation on the electrolytes after cyclic sweeps is required to make a solid conclusion.

Based on these results, neither band gap nor dielectric constant of the oxide coating has a dominating effect on its ability to stabilize the aqueous system. The chemical reactivity of the coating material against the electrolyte is the crucial factor. Studies of other high  $\kappa$  oxides, such as silicon nitride and hafnium silicate, can help to confirm this hypothesis.

## References:

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