Surface Analysis of Sulfur Coated Electrides For Enhanced Stability

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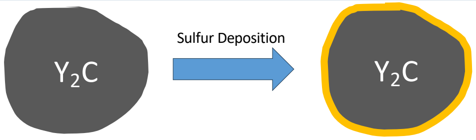
Introduction



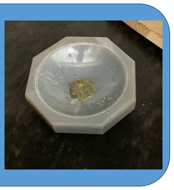
To meet increasing energy demands, new materials must be researched and characterized. One such material is electrides: inorganic crystals that contain electrons in place of anions. Some electrides crystallize in layers, which results in a low work function, high anisotropic conductivity, and high energy electrons, making them highly interesting for applications in batteries and catalysis.[1,2,3] Unfortunately, the same high energy electrons that make the material useful also contribute to swift degradation in the presence of oxygen.

Surface coatings have been used to stabilize some electrides, but have yet to be applied to the layered electride Y_2C.[4] Y_2C is a promising electride as it can be used as an electrode in batteries. However, the electride is oxidized in air, hindering its long-term stability. I propose using a surface coating of sulfur to pacify the high-energy surface. The ionic radius of sulfur is too large to be intercalated into the material, yet sulfur is soluble in electride stable solvents. Additionally, the layer created by sulfur is homogenous. By tuning parameters such as temperature, annealing time, and soaking time, the properties of the surface layer can be adjusted. The tuned surface coating can be used in a wide array of batteries, optical devices, catalysts, or capacitors.

Methods

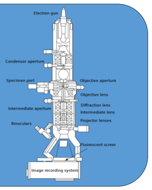
Preparation of Sulfur Layer

Sulfur is melted in a pestle at variable temperature in a fume hood. After the sulfur is completely melted, Y_2C is directly added to the sulfur and then ground. The suspension is allowed to cool before the Y_2C powder is transferred to a glove box. The powder is added to a solution of toluene and allowed to soak before experiments are conducted on the layer.



Transmission Electron Microscopy (TEM)

Elemental analysis of the Y_2C pellets is conducted through TEM. TEM probes the pellets in an air free environment, which ensures minimal exposure to oxygen. The relative abundance of each element can be calculated with energy dispersive X-ray spectroscopy.



X-Ray Diffraction (XRD)

XRD is used to evaluate the crystallin properties of the material. Time resolved XRD was used to evaluate whether a surface layer of sulfur prevented the degradation of crystalline Y_2C into its amorphous oxidized form.

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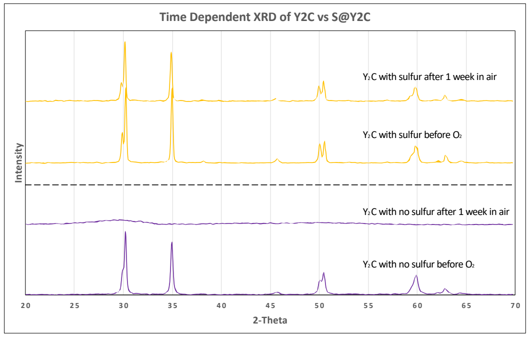
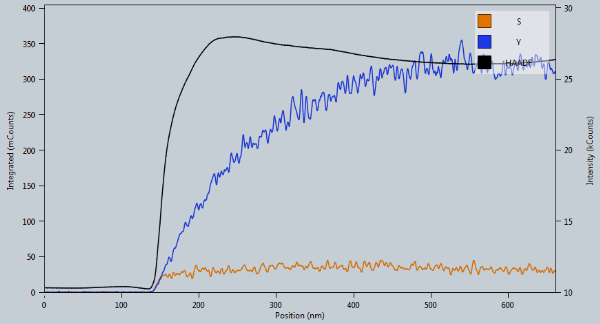
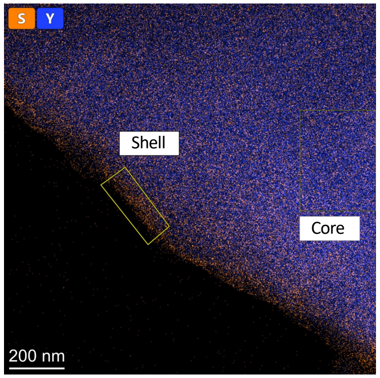
Results

XRD of Sulfur Coated Y2C

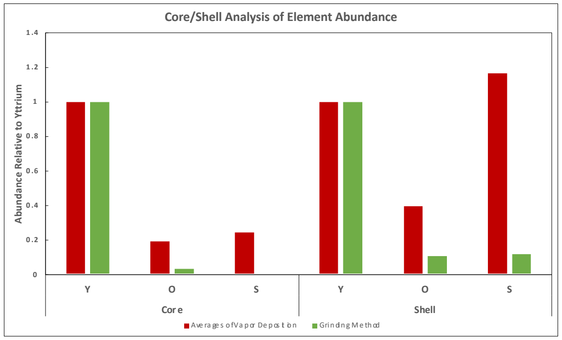


Depth Profile of Sulfur Coated Y2C





Core/Shell Analysis of Elemental Abundances



Conclusion/Future Directions

Based on the TEM data collected, it is clear that the presence of oxygen in the core of the system has been reduced. Oxygen is still present in both the core and shell of the sulfur-yttrium carbide system, but the new method has been successful in preventing the formation of yttrium oxide. When preparing future samples of sulfur coated yttrium carbide, grinding in liquid sulfur should be employed over vapor phase deposition in order to minimize exposure to oxygen. Future experiments will include using XPS to measure the thickness and uniformity of the sulfur layer with precision. After XPS is performed, various experiments can be performed to reduce the thickness of the sulfur layer to a minimum. These include using solvent blends of toluene with other nonpolar solvents such as xylene, benzene, or hexanes. Performing the deposition at a cooler temperature may reduce the intercalation of sulfur. Additionally, modulating the soaking time of the samples in solvent will allow better understanding of the parameters that control surface layer thickness in the core/shell system.

Acknowledgements

1) Takeshi Tojigamori; Matsui, N.; Suzuki, K.; Hirayama, M.; Abe, T.; Kanno, R. Fluorination/Defluorination Behavior of Y_2c in Fluoride-Ion Battery Anodes. *ACS Appl. Energy Mater.* **2024**, *7* (3), 1100–1108. https://doi.org/10.1021/acsaem.3c02613.
2) Druffel, D. L.; Pawlik, J. T.; Sundberg, J. D.; McRae, L. M.; Lanetti, M. G.; Warren, S. C. First-Principles Prediction of Electrochemical Electron–Anion Exchange: Ion Insertion without Redox. *J. Phys. Chem. Lett.* **2020**, *11* (21), 9210–9214. https://doi.org/10.1021/acs.jpclett.0c02266.
3) Zhang, Z.; Jiang, Y.; Li, J.; Miyazaki, M.; Kitano, M.; Hideo Hosono. A 2D Ba_2N Electride for Transition Metal-Free N_2 Dissociation under Mild Conditions. *J. Am. Chem. Soc.* **2023**. *145* (45)24482-24485 https://doi.org/10.1021/jacs.3c09362.
4) Faseela, K. P.; Ye Ji Kim; Kim, S.-G.; Sung Wng Kim; Baik, S. Dramatically Enhanced Stability of Silver Passivated Dicalcium Nitride Electride: Ag-ca_2N. *Chem. Mater.* **2018**, *30* (21), 7803–7812. https://doi.org/10.1021/acs.chemmater.8b03202.

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