Powering Zinc-Air Batteries with Porphyrin-Based Covalent Organic Frameworks

NEBRASKA CENTER FOR ENERGY SCIENCES RESEARCH

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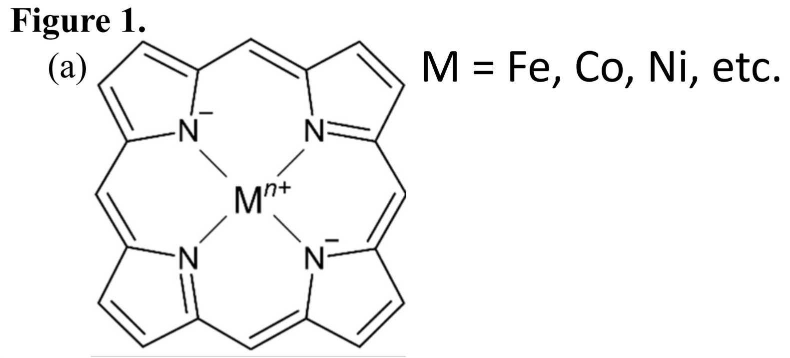
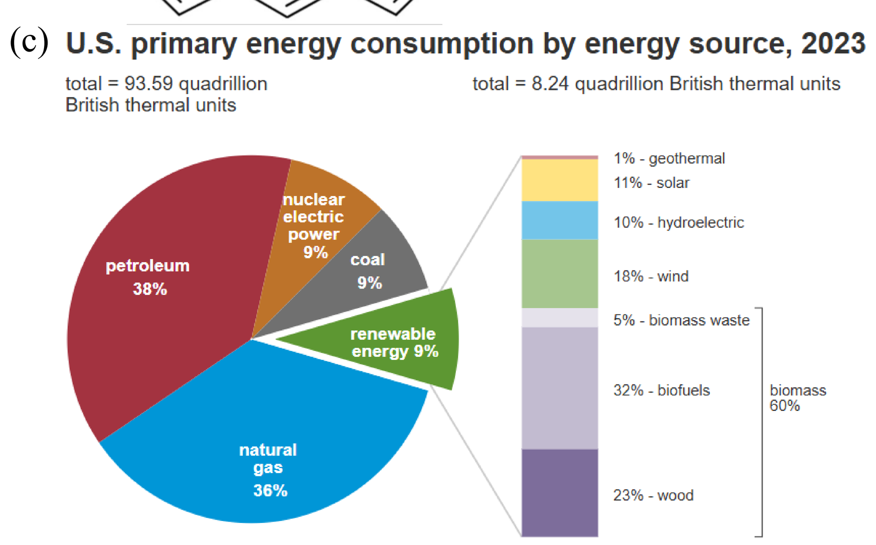
Motivation

Rechargeable Zinc-Air Batteries (ZABs) are emerging as a compelling alternative to traditional battery technology due to their unique combination of high energy density, sustainability, and safety. This makes the technology suitable for many applications such as in energy storage, electric vehicles, and portable electronics. ZABs have many applications and a wide range of potential, but stability at the zinc electrode and the lack of a bifunctional catalyst at the air electrode are two major hang ups in the development of the battery to the mainstream. With solutions to these issues, large scale applications of ZABs offer a step forward in green and sustainable energy.

The stability of zinc is an important topic of research; however, the catalytic activity for both oxygen reduction (ORR) and oxygen evolution (OER) are investigated for porphyrin-based polymers such as pTAPP [poly(5,10,15,20 – tetrakis(4-aminophenyl)porphyrin)] in this project. pTAPP can have a single atom active center through coordination of a transition metal which exhibits a $M\text{-}N_4$ moiety. These moieties have shown a lot of promise for ORR and potentially OER activity [3].

Figure 1.





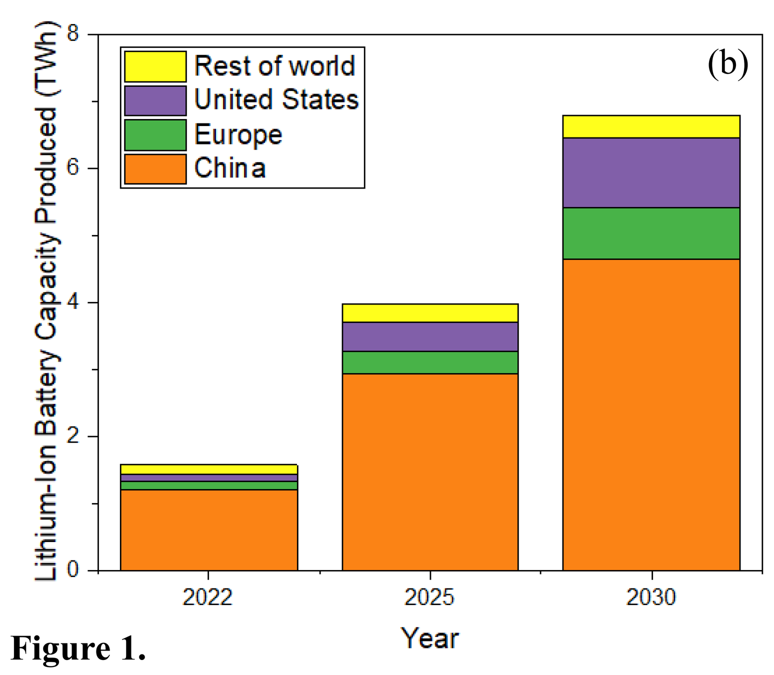
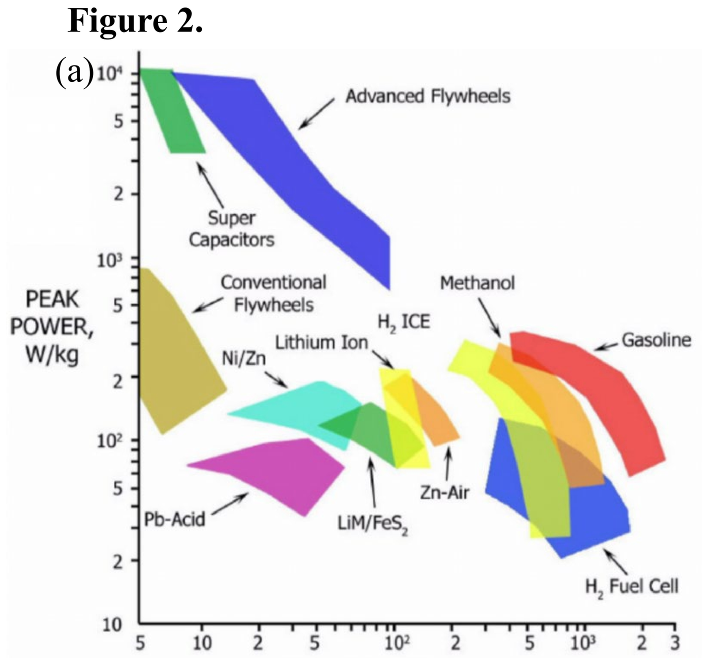
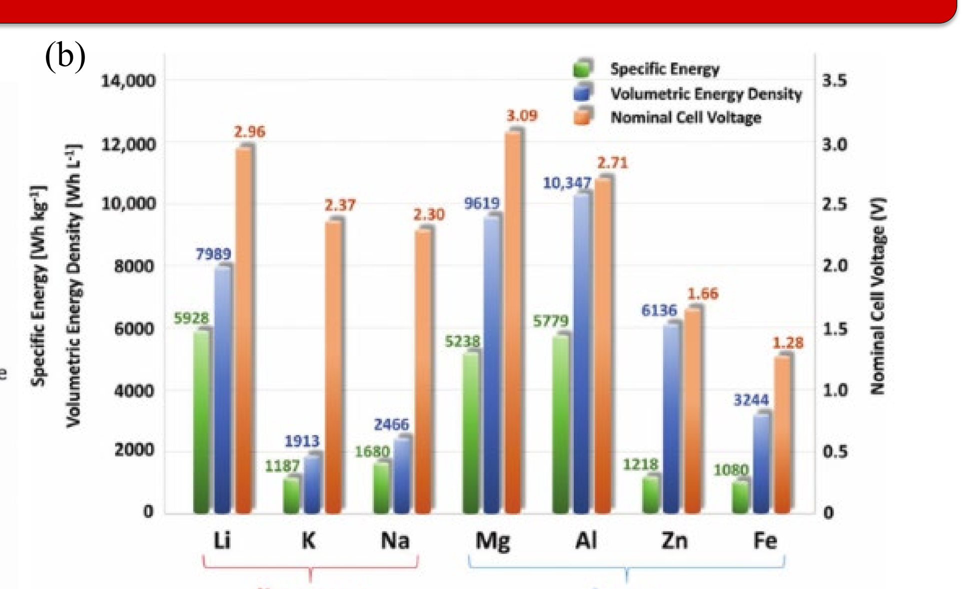


Figure 1.
(a) The backbone of a porphyrin ring with a metal center. (b) The energy consumption (2,415 TWh) distribution in the United States [1] and the (c) lithium-ion battery consumption given in TWh [2].

Zinc-Air vs. Other Batteries

Figure 2.





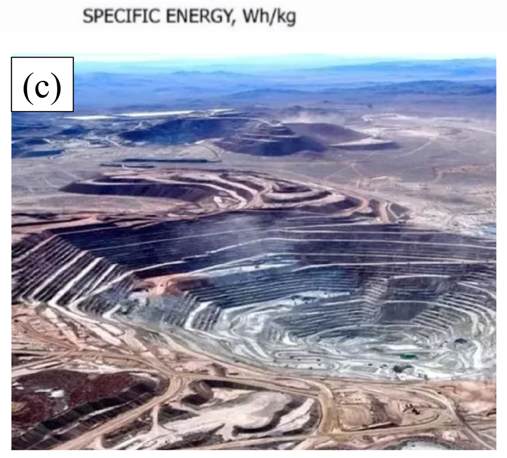


Figure 2.
(a) A Ragone Plot for many different energy sources, such as electrochemical cells, fuels, capacitors, and even flywheels. [5]

(b) Comparison between Zinc-Air and other metal-air batteries. This comparison is done based on the Specific Energy, Cell Voltage, and Volumetric Energy Density [6].

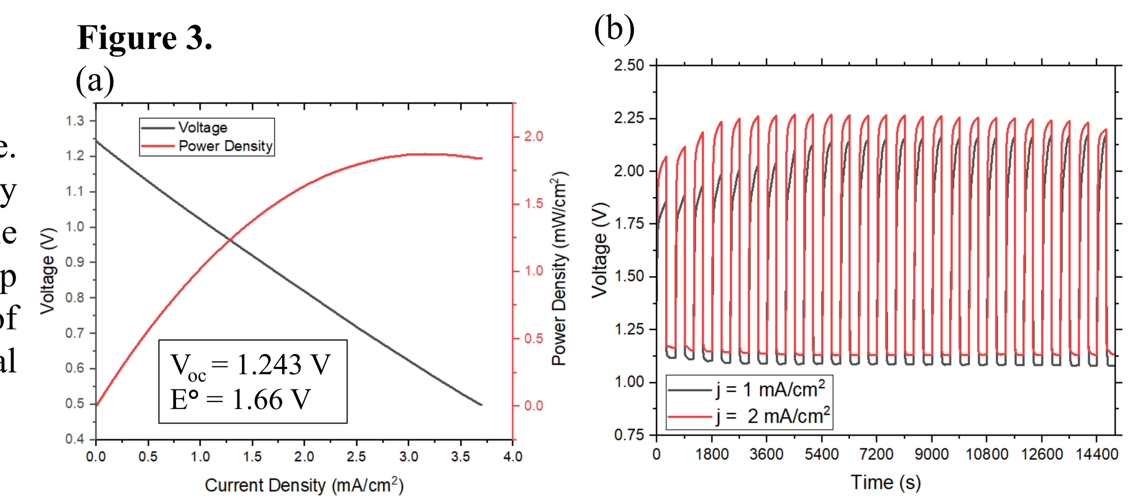
(c) Lithium-metal mine, displays environmental impact of quarry [8]

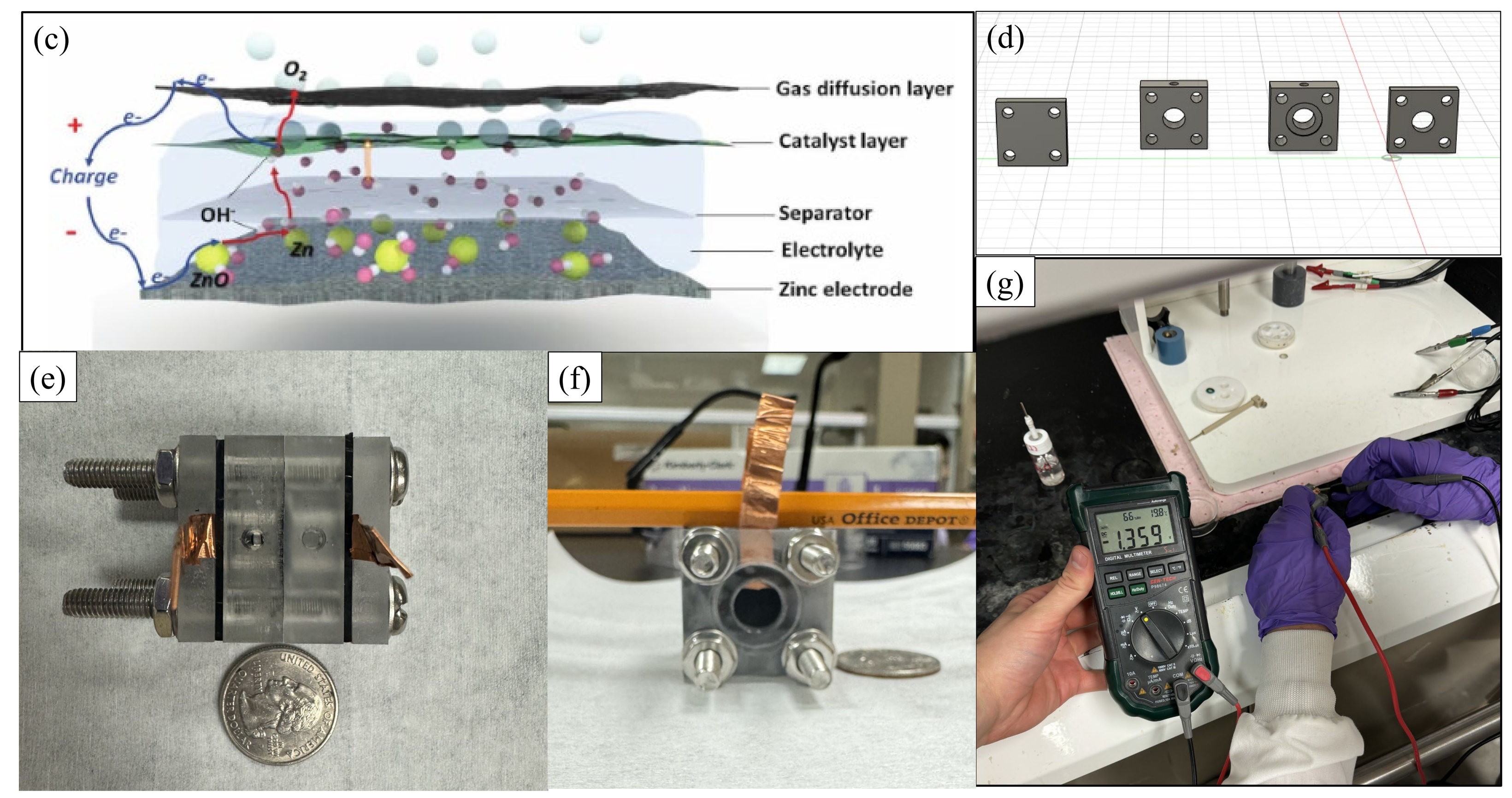
Zinc-air batteries have both a high energy density and a lower environmental hazard compared to lithium-ion batteries which have similar energy storage capabilities. The components of lithium-ion batteries require labor intensive mining processes and lithium is much scarcer than zinc.

Rechargeable ZAB Model and Testing

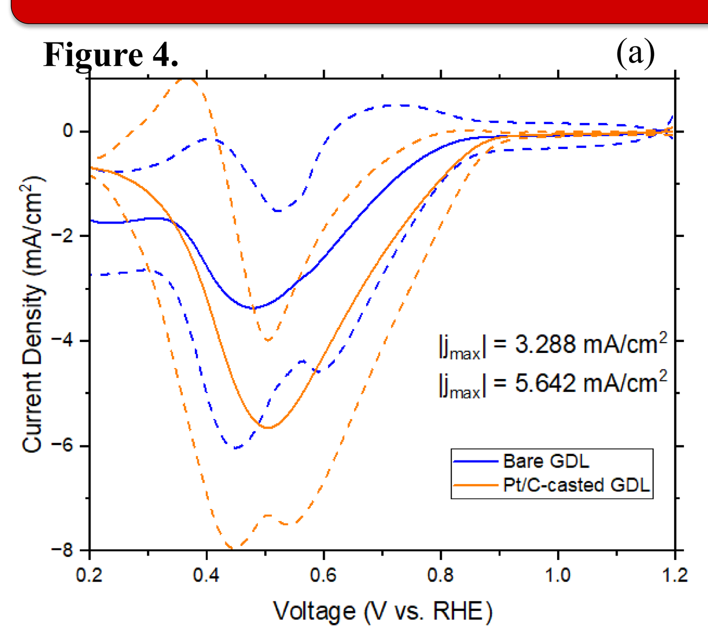
The battery was made with machined acrylic pieces with the purpose of holding the zinc electrode, gas diffusion layer (GDL), a membrane separator, and copper tape current collectors without leaking electrolyte. After the cell passed leak tests, preliminary tests were run to analyze stability on a basic zinc-air battery prototype.

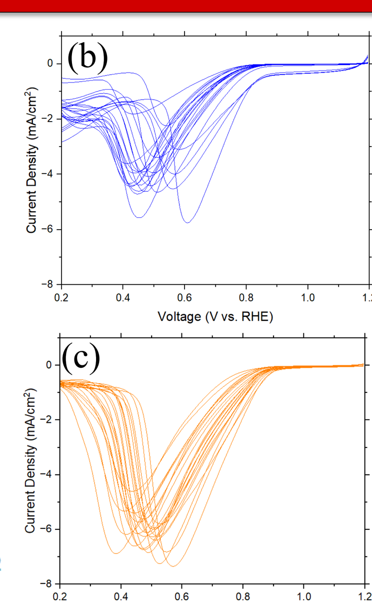
Figure 3.
(a) Polarization Curve
(b) Galvanostatic Charge-Discharge.
(c) Depiction of Zn-Air Battery components [4]. (d) Fusion 360 file used to assemble the battery. (e) Top view and air-electrode-view (f) of battery. (g) Open circuit potential measured by multimeter.

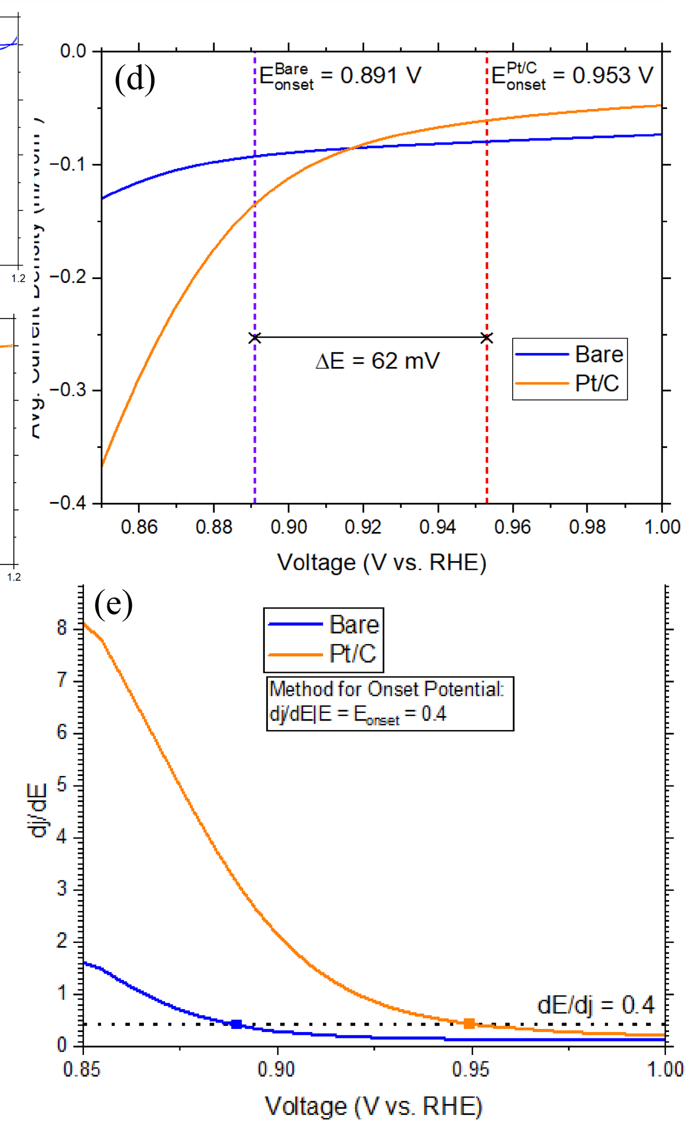




Control Testing







Pt/C-casted GDL and Bare GDL were tested in a three-electrode setup in a potential window from 0.2 V to -0.8V at a scan rate of 20 mV/s.

Figure 4.
(a) Mean current density for each cloth with 95% confidence interval indicated by dashed lines. (b) and (c) are 'spaghetti' plots showing all 23 samples for bare GDL (blue) and Pt/C-casted GDL (orange).
(d) The onset potential of the average current density graph for Pt/C and bare GDL is found through numerically determining the slope at each point through (e).

$$\frac{dj}{dE}\Big|_{E = E_{onset}} = 0.4 \quad E = 1.175 \text{ V vs RHE} \quad |\eta| = E° - E_{onset}$$

$$|\eta_{Pt/C}| = 0.223 \text{ V} \qquad |\eta_{Bare}| = 0.285 \text{ V}$$

POR-COFs

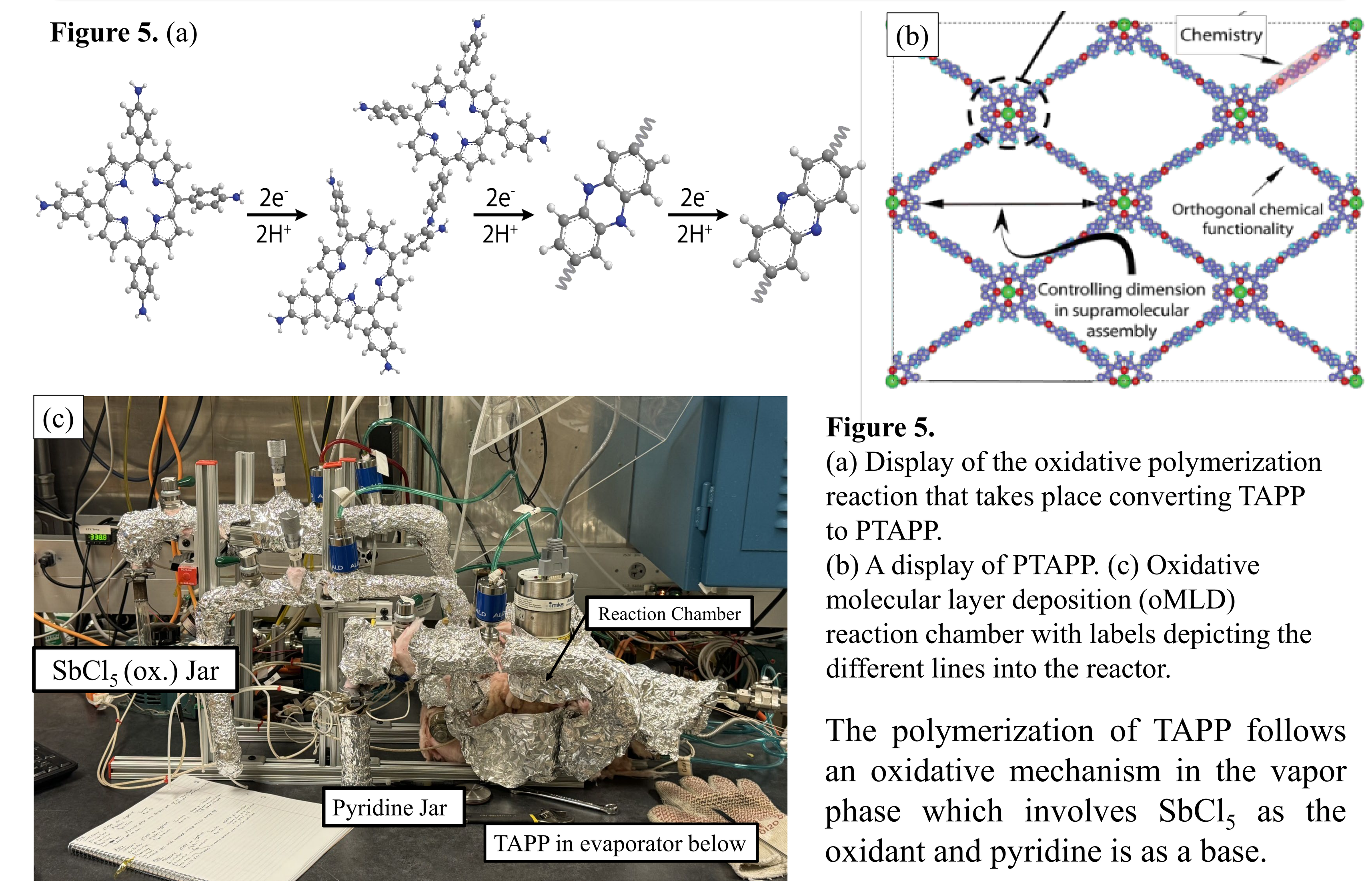


Figure 5.
(a) Display of the oxidative polymerization reaction that takes place converting TAPP to PTAPP.
(b) A display of PTAPP. (c) Oxidative molecular layer deposition (oMLD) reaction chamber with labels depicting the different lines into the reactor.

The polymerization of TAPP follows an oxidative mechanism in the vapor phase which involves $SbCl_5$ as the oxidant and pyridine is as a base.

Future Works

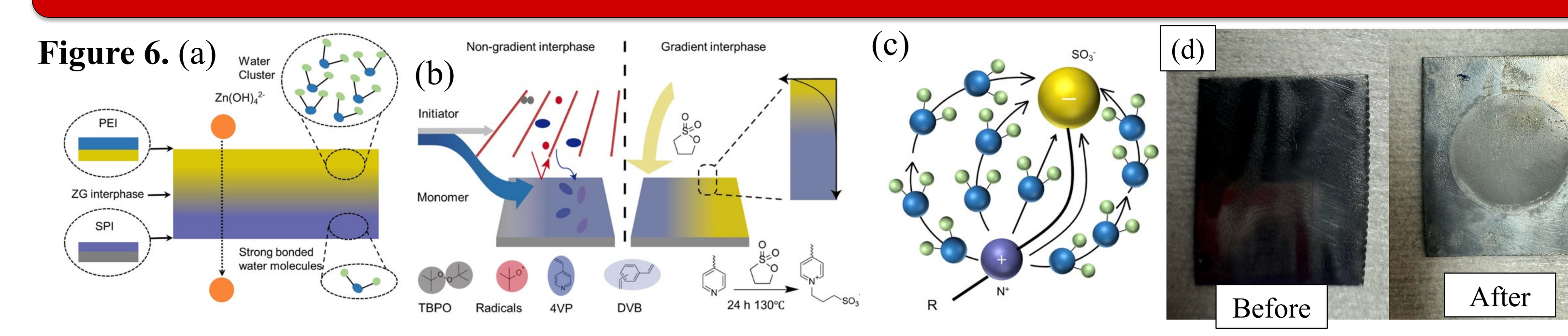


Figure 6. A zwitterionic polymer (a-c) will be investigated to reduce deterioration of the zinc electrode (d). This recipe [7] consists of a zwitterionic polymer synthesized by an iCVD reactor. This polymer has been shown to effectively passivate the zinc electrode to hydrogen evolution leading to a more stable, longer-lasting zinc electrode.

Acknowledgements

This work was supported by the Nebraska Public Power District through the Nebraska Center for Energy Sciences Research at the University of Nebraska-Lincoln.

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