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## Student Abstracts: Chemistry at NREL

**Conductivity Measurements of Synthesized Heteropoly Acid Membranes for Proton Exchange Membrane Fuel Cells.** BRENNNA HALEY (University of Northern Colorado Greeley, CO 80639) DR. JOHN TURNER (National Renewable Energy Laboratory, Golden, CO, 89401)

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Fuel cell technology is receiving attention due to its potential to be a pollution free method of electricity production when using renewably produced hydrogen as fuel. In Proton Exchange Membrane (PEM) fuel cell  $H_2$  and  $O_2$  react at separate electrodes producing electricity, thermal energy, and water. A key component of the PEM fuel cell is the membrane that separates the electrodes. DuPont's Nafion<sup>®</sup> is the most commonly used membrane in PEM fuel cells; however, fuel cell dehydration at temperatures near 100°C, resulting in poor conductivity, is a major hindrance to fuel cell performance. Recent studies incorporating heteropoly acids (HPAs) into membranes have shown an increase in conductivity and thus improvement in performance. HPAs are inorganic materials with known high proton conductivities. The primary objective of this work is to measure the conductivity of Nafion, X-Ionomer membranes, and National Renewable Energy Laboratory (NREL) Developed Membranes that are doped with different HPAs at different concentrations. Four-point conductivity measurements using a third generation BekkTech<sup>®</sup> conductivity test cell are used to determine membrane conductivity. The effect of multiple temperature and humidification levels is also examined. While the classic commercial membrane, Nafion, has a conductivity of approximately 0.10 S/cm, measurements for membranes in this study range from 0.0030 - 0.58 S/cm, depending on membrane type, structure, the HPA, and the relative humidity. In general, the X-ionomer with  $H_6P_2W_{21}O_{71}$  HPA gave the highest conductivity and the Nafion with the 12-phosphotungstic ( $PW_{12}$ ) HPA gave the lowest. The NREL composite membranes had conductivities on the order of 0.0013 - 0.025 S/cm.

**Ordered Nucleation Sites for the Growth of Zinc Oxide Nanofibers.** JENNIFER WANG (Rice University Houston, TX 77005) DAVID GINLEY (National Renewable Energy Laboratory, Golden, CO, 89401)

Organic photovoltaics (OPVs) offer a promising route to low cost photovoltaic (PV) technology that can be inexpensively manufactured on a large scale for use in power generation and commercial products. Solar power conversion efficiencies of laboratory scale OPV devices have recently reached ~5%; however, projected efficiencies of at least 10% will be required for commercialization. An analogous approach that has arisen recently that can potentially increase efficiencies employs metal oxide

semiconductors as the electron acceptor, creating a hybrid organic-inorganic device. This approach offers the advantage that the conduction band of the oxide can be tuned in a systematic way through doping, thus potentially achieving higher photovoltages for the device. Additionally, nanostructures of these materials can be easily grown from precursor solutions, providing a technique to precisely control the nanoscale geometry. This work focuses on using ZnO, which is known to have high electron mobility ( $>10 \text{ cm}^2/\text{Vs}$ ), as the electron acceptor. Nanofibers of ZnO can be grown from precursors such as zinc acetate or zinc nitrate to form arrays of nanofibers into which a conjugated polymer can be intercalated to form a composite PV device. The morphology of the nanofiber array is critical to the performance of the device, but current methods of nanofiber growth from a flat, polycrystalline nucleation layer allow for little morphological control. To overcome this limitation, we have created ordered arrays of ZnO nucleation sites with controllable size and spacing. Toluene solutions of diblock copolymer micelles with  $\text{ZnCl}_2$  incorporated into the micellar cores were spin-coated onto glass substrates and etched with an  $\text{O}_2$  plasma to yield hexagonally ordered arrays of ZnO nanoparticles that functioned as nucleation sites. Changing the concentration of  $\text{ZnCl}_2$  and the molecular weight and ratio of the diblock copolymer resulted in systematic variation in the size and spacing of the nucleation sites. Thermal anneal treatment provided further modification of the nucleation layer, from which ZnO nanofibers were successfully grown from solution, although at present it is not known if the geometry of the as-grown ZnO nanofibers precisely reflects that of the underlying nucleation layer. This work provides a simple and useful method for potentially controlling the nucleation of ZnO nanofibers to be used in hybrid ZnO/organic nanocomposite PV devices.

#### **Photoelectrochemical Characterization of Gallium Indium Nitride Phosphide.**

CALONDRA COLVIN (Baylor University Waco, TX 76706) JOHN TURNER (National Renewable Energy Laboratory, Golden, CO, 80401)

Hydrogen gas is evolved from the surface of Gallium Indium Nitride Phosphide (GaInNP) when placed in aqueous solution, along with a platinum counter electrode under an applied current. The success of hydrogen as an energy carrier is dependent on both how well the semiconductor material, in this case gallium indium nitride phosphide, can hold up to corrosion in aqueous solution, along with how efficiently it produces hydrogen. The focus of our research is quantizing both of these abilities for GaInNP by measuring the flat band potential, band gap and corrosion susceptibility. Band gap is calculated with data from photocurrent spectroscopy, and flat band potential using illuminated open circuit potentials, photocurrent onset measurements and Mott-Schottky analysis values. Although the band gap of GaInNP lies above the necessary 1.8 eV, valence band values failed to realize potentials capable for water splitting. Ultimately, to split water the sample would need both a valence band more positive of the oxygen redox potential, and a conduction band more negative of the hydrogen redox potential. GaInNP fulfills the hydrogen part of this requirement but not the oxygen complement. Durability tests showed a steady, minimal amount of corrosion occurring at the electrode surface over a period of 24-hours. Future work includes investigating the effects the quantization techniques using atomic force microscopy and profilometry. Corrosion results in fragmentation of the electrode surface, so by measuring the elemental composition using inductively coupled plasma atomic emission analysis, specific changes will be realized.

**Silicon Nitride for Direct Water-Splitting and Corrosion Mitigation.** JEFF HEAD (Colorado State University Fort Collins, CO 80120) JOHN TURNER (National Renewable Energy Laboratory, Golden, CO, 89401)

Today's fossil fuels are becoming harder to obtain, creating pollution problems, and posing hazards to people's health. One alternative to fossil fuels is hydrogen, capable of serving as a clean and efficient energy carrier. Certain semiconductors are able to harness the energy of photons and direct it into water electrolysis in a process known as photoelectrochemical water splitting. Triple junction devices integrate three semiconductors of different band gaps resulting in a monolithic material that absorbs over a broader spectrum. Amorphous silicon (a-Si) is one such material that, when stacked in tandem, possesses water-splitting capabilities. Even though a-Si is capable of splitting water, it is an unstable material in solution and therefore requires a coating to protect the surface from corrosion. A stable, transparent material that has the potential for corrosion protection is silicon nitride. In this study, silicon nitride thin films were grown using DC magnetron sputtering with varying amounts of argon and nitrogen added to the system. X-ray diffraction indicated amorphous silicon nitride films. Current as a function of potential was determined from cyclic voltammetry measurements. Mott-Schottky analysis showed variation in flatband potentials with n-type behavior. Absorption and transmission measurements indicate variation in band gap values ranging from 1.90 to 4.0 eV. Corrosion measurements reveal that the silicon nitride samples exhibit both p-type and n-type behavior. Photocurrent over a range of potentials was greater in samples that were submerged in acidic electrolyte. Silicon nitride shows good stability in acidic, neutral, and basic solutions, indicating a good material for corrosion mitigation.