Enhancing Proton Exchange Membrane Functionality with Biomolecules

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Integrating biomolecules with proton exchange membranes (PEM), such as Nafion® (Dupont), can help to address some of the issues associated with PEM efficiency, such as proton leakage and water loss. Biomolecules, such as membrane proteins, can be reconstituted into biosynthetic membranes. Using an ABA (hydrophilic-hydrophobic-hydrophilic) triblock copolymer, we can mimic a natural lipid membrane in a single chain. With its amphilic properties, the ABA triblock copolymer can also enable large-area monolayer formation across an air-water interface using Langmuir-Blodgett (LB). By mimicking a natural cell membrane, block copolymers also enable proper protein refolding and sustained functionality. We have successfully inserted several membrane proteins into large-area polymer membranes, including the light-activated proton pump, bacteriorhodopsin (BR) and the pH/voltage-gateable porin, Outermembrane Protein F (OmpF). We have confirmed the insertion of proteins into a floating polymer film on the air-water interface of the LB trough by transmission electron microscopy (figure 1) of cysteine-labeled OmpF conjugated with 10nm colloidal gold beads. Using the perpendicular dipping method in a LB trough, we have also deposited hybrid protein/polymer films onto a variety of substrates including Nafion®, gold, quartz, and silicon. Nafion®, despite having a hydrophobic Teflon®-like backbone, has hydrophilic sulfonic acid side chains that can interact with the hydrophilic head of a lipid bilayer or block copolymer. We have also confirmed the deposition of bacteriorhodopsin, in the form of purple membrane fragments of the bacteria *Halobacterium Halobium*, through UV-vis spectrophotometry. We have also demonstrated protein function of bacteriorhodopsin deposited onto a PEM. Oriented PM, through the asymmetric biotinylation of the extracellular side, has indicated the ability to prevent proton loss across Nafion® 117 (Figure 3). Furthurmore, increased proton pumping activity is witnessed in the presence of light, indicating the function of light-dependent protein activity. In a conventional fuel cell, the following reaction takes place on the cathodic side:

$$0_2 + 4H^+ + 4e^- \rightarrow 2H_20.$$

By reducing the loss of protons through light-actuated protein activity, chemical reactions in the fuel cell can be made more efficient. Furthermore, water loss requires more water to be pumped into the fuel source of a hydrogen fuel cell to offset water loss across the PEM and as water gets dragged with the protons across the PEM, the cathode catalyst sites can become flooded, reducing oxygen access and lowering the effective voltage. Block copolymers, like lipid bilayers, provide a natural impediment to water, and when functionalized with proteins that act as proton pumps, or ion channels, PEMs can maintain their conductive properties while reducing electro-osmotic drag (EOD) of water.

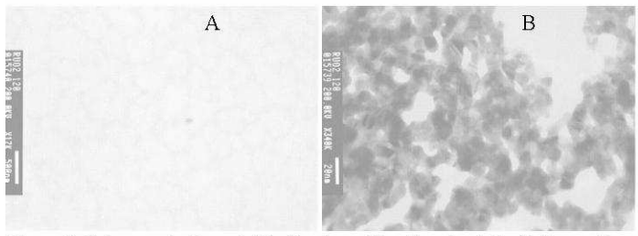

Figure 1. Polymer only shown in 1A. Cys-tagged OmpF conjugated with Nanogold particles shown in 1B.

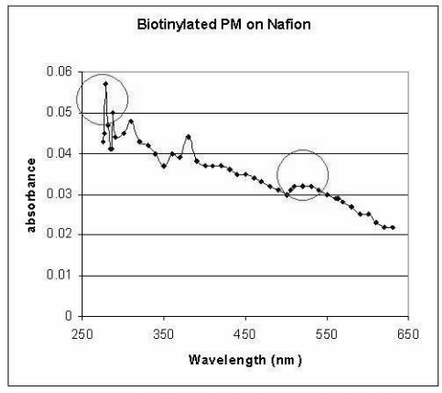

Figure 2. Characteristic absorbance peaks near 563 nm and 278nm of biotinylated PM adsorbed to Nafion.

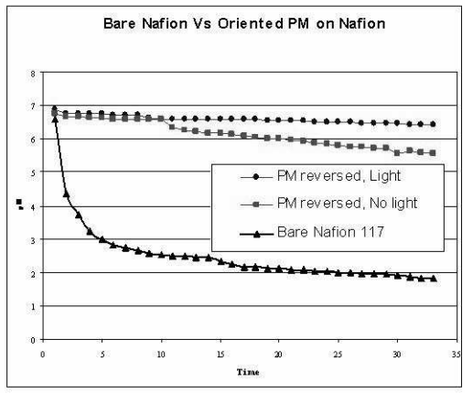

Figure 3. Proton Reversal trials across oriented hybrid protein/Nafion films in light and dark, compared to Nafion films without BR.