Towards the Development of an Ethanol bioanode employing PQQ as a Coenzyme in Tetrabutylammonium Bromide Treated Nafion® Membrane

Becky L. Treu and Shelley D. Minteer
Department of Chemistry
Saint Louis University
3501 Laclede Ave.
St. Louis, MO 63103

A fuel cell is a battery that can be regenerated with the addition of more fuel to the cell the chosen. A biofuel cell uses biocatalysts for the conversion of chemical energy to electrical energy. A bioanode comprises half of a biofuel cell and oxidizes the specific fuel. Previous research in our group has focused on ethanol based biofuel cells that employ the use of enzymes immobilized at the surface of the electrodes as fuel cell catalysts. Immobilized enzymes will remain active and not denature since the pore restricts the enzyme. In order to increase the lifetime and activity of the bioanode Nafion treated with tetrabutylammonium bromide (TBAB) salts is used to immobilize enzymes at the electrode surface to be employed for biofuel cell applications.(1-3)

The current enzymatic system chosen involves immobilizing NAD^+-dependent alcohol dehydrogenase (ADH) in a salt extracted TBAB/Nafion membrane in order to oxidize ethanol to aldehyde. It has shown as problematic for several reasons. NAD^+ has a high overpotential so an electrocatalyst layer is necessary to decrease the potential and increase the power output. Previous research employs methylene green as the electrocatalyst layer due to its optimal electrocatatlytic properties. The electrocatalyst layers are not as conductive as a carbon electrode and add complexity to the bioanode. Another problem associated with NAD^+-dependent ADH is during the redox reaction occurring at the bioanode NAD^+-dependent ADH reduces NAD^+ to the neutral species NADH causing leakage of the coenzyme NAD^+ from the membrane. Therefore, NAD^+ is labile and has a short lifetime in the biofuel cell. Replacing NAD+-dependent ADH with PQQ-dependent ADH will eliminate the problems associated with the current enzymatic system. PQQ is the coenzyme of PQQ-dependent ADH it remains electrostatically attatched to PQQ-dependent ADH and therefore the enzyme will remain in the membrane leading to an increased lifetime and activity for the biofuel cell. Also, PQQ-dependent ADH eliminates the need for an electrocatalyst layer therefore simplifying the process of forming high surface area bioanodes. The goal of this research is to isolate PQQ-dependent alcohol dehydrogenase from gluconobacter species in order to replace NAD^+-dependent alcohol dehydrogenase.

Pyrroloquinoline quinone (PQQ)-dependent alcohol dehydrogenase (ADH) has been chosen to replace NAD^+-dependent ADH as a fuel cell catalyst due to its unique electrochemistry. In order to replace the current enzymatic system a crude PQQ-dependent ADH must be extracted from commercially available gluconobacter.(4) Cyclic voltammetry is used to investigate the electrochemistry of the immobilized PQQ-dependent ADH present at the surface of a glassy carbon electrode. Sample data shows an enhancement in electrical current for a sample bioanode coated with extracted PQQ-dependent PQQ-dependent ADH immobilized in TBAB/Nafion is actively oxidizing ethanol creating an electrochemical current larger than that of TBAB/Nafion alone.

After successful extraction of active enzyme carbon paper anodes are fabricated then coupled with a Vulcan XC-17 cathode with 20% Pt loading to test open circuit potential, current, and power of the complete biofuel cell. Preliminary data has shown a maximum open circuit potential of 1.0 V, maximum power increase of 222% (as shown in Figure 2) and an overall lifetime increase of at least 113 days compared to the NAD^+-dependent ADH bioanode. The PQQ-dependent ADH bioanode out performs the NAD^+-dependent bioanode.

References

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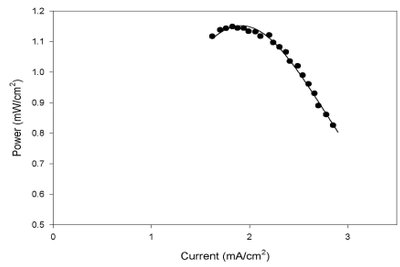

Figure 1
Power curve for 2:1 NAD^+-dependent ADH to TBAB/Nafion Membrane
Fuel containing 1mM NAD^+/1mM ethanol/phosphate buffer pH 7.15

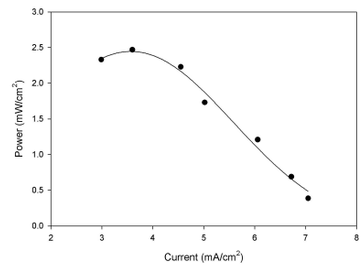

Figure 2
Power Curve for 2:1 PQQ-Dependent ADH to TBAB/Nafion Membrane
Fuel containing 1mM PQQ/1mM ethanol/phosphate buffer pH 7.15