

## Hydrogen production by alkaline membrane water electrolysis

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Water electrolysis is an efficient and reliable method to produce hydrogen from renewable energy sources without any carbon dioxide (CO<sub>2</sub>) or carbon monoxide side products. There are three types of water electrolysis processes commercially available: alkaline water electrolysis using a liquid electrolyte, PEM water electrolysis and solid oxide water electrolysis. Alkaline liquid electrolyte water electrolysis, (1) and proton exchange membrane (PEM) water electrolysis (2) are operated at low temperatures (50-150°C) and are more suitable for portable and on-site applications.

Alkaline electrolyzers use concentrated liquid alkali electrolyte (typically 10 M KOH) that it is very corrosive and can form insoluble carbonates in contact with CO<sub>2</sub> in the air. These carbonates can easily precipitate in the porous electrodes blocking the access of water to the catalyst surface and of hydrogen and oxygen gases from the catalyst, and hence negatively affecting the electrolyzer performance and durability. For PEM electrolyzers, they use perfluorinated cation exchange polymer electrolyte membranes (i.e. Nafion®, Flemion®, Aciplex-S®) that are expensive and the electrolyzers require the use of expensive noble metal catalysts since they operate in acidic environments.

Alkaline membrane water electrolysis could offer several advantages over conventional alkaline or PEM electrolyzers because the use of non-corrosive solid electrolyte allows a differential pressure to be applied across the membrane and the alkaline environment makes it possible to use non-platinum group metal catalysts for hydrogen and oxygen evolution reactions.(1)

In this work, we have demonstrated the viability of an alkaline membrane (AEM) water electrolyzer using a polysulfone-based anion exchange membrane (functionalized with quaternary benzyl trimethylammonium hydroxide groups) and lead ruthenate pyrochlore electrocatalyst for the oxygen evolution reaction. The same AEM polymer was used as electrode binder/ionomer to allow hydroxide conduction in the electrodes.

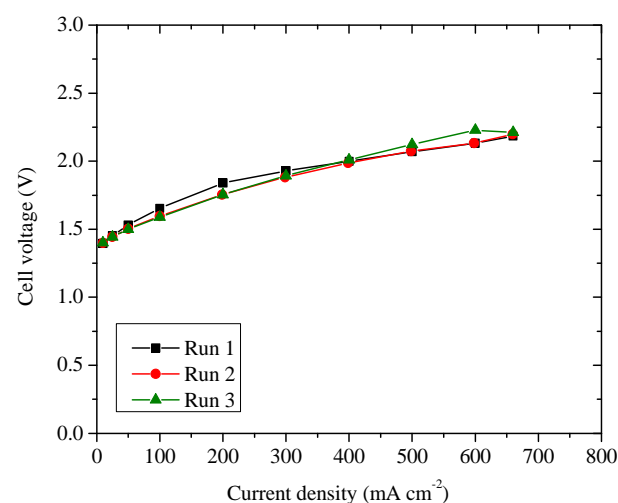
Polysulfone was chloromethylated via the Friedel-Crafts reaction following the Avram procedure.(3) The chloromethylated PSF (CMPSF) was then reacted with trimethylamine (TMA) to obtain quaternary ammonium anion exchange ionomer (PSF/TMA<sup>+</sup>Cl<sup>-</sup>). The PSF-TMA<sup>+</sup>Cl<sup>-</sup> film was ion-exchanged to hydroxide form before assembling in the electrolyzer, by immersing in 1 M KOH solution at room temperature overnight.

Membrane electrode assemblies (MEAs) with an active area of 25 cm<sup>2</sup> were prepared by sandwiching an AEM between two gas diffusion electrodes (GDE). Cathode was prepared by applying Pt black electrocatalyst on a carbon paper (GDL). The anode was prepared similarly applying lead ruthenate pyrochlore on a porous titanium sheet. The catalyst loadings were approximately 2.5 mg/cm<sup>2</sup> for both electrodes. The experiments were conducted in a modified single fuel cell hardware (Fuel Cell Technologies, Inc.); the anode graphite plate was replaced by a titanium plate to avoid

carbon corrosion.

The electrolysis of ultrapure water at 1.80 V and 50 °C resulted in a current density of 400 mA cm<sup>-2</sup> (see Fig 1). We also found the diffusion of carbon dioxide inside the membrane and the water storage tanks negatively affected the electrolyzer performance. The formation of carbonate and bicarbonate anions inside the membrane and the electrodes increased the membrane resistance (as found using impedance spectroscopy) and electrode resistance (due to lower ionic conductivity in the electrodes). The stability of the electrolyzer was greatly improved by minimizing carbon dioxide intrusion into the electrolysis cell.

<sup>1</sup>H NMR, <sup>13</sup>C NMR, two-dimensional NMR homonuclear correlation spectroscopy (COSY), and <sup>1</sup>H-<sup>13</sup>C heteronuclear multiple quantum correlation (HMQC) spectroscopy were employed to investigate the polymer structure before and after use in the electrolyzer. Backbone degradation after continuous operation for 24-48 hours was detected. Although there are several problems to be solved, like the chemical degradation of the ionomer and the poor mechanical integrity of the membranes, the use of alkaline membranes is promising for low-cost, high purity scalable hydrogen production.



**Figure 1.** Polarization curves for electrolysis of ultrapure water at 50°C using an AEM.

### References:

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