Electrode optimization for efficient hydrogen production using an SO_2-depolarized electrolysis cell

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Abstract

The hybrid sulfur (HyS) cycle offers an alternative route to hydrogen and sulfuric acid production using the SO_2-depolarized electrolysis (SDE) cell. This work reports the most efficient SDE operation to date at high sulfuric acid concentrations (~ 60 wt%) achieved through the optimization of operating conditions and cell components. We observed that open porosity in the porous transport media (PTM) plays a significant role in SDE performance as it enables efficient acid removal from the catalyst layer. The combination of membrane electrode assembly (MEA) components, such as Sulfonated Diels Alder Poly(phenylene) (SDAPP) membranes and electrodes prepared using SGL 29BC PTM, and operating conditions (103.4 kPa_{gauge} at 125 ºC) yielded electrolysis potentials < 700 mV at 500 mA/cm^2 and acid concentrations > 60 wt%.

Keywords: hybrid sulfur cycle, electrolysis, sulfur dioxide, hydrogen generation, catalysis, high pressure

Introduction

Hydrogen is a key energy carrier to facilitate decarbonization across multiple sectors of the energy economy. Once made, hydrogen can serve as an energy storage medium for subsequent power generation or as a carbon-free feedstock for many different commodity products.[1] Hydrogen may also be used to carry clean energy from renewables or nuclear reactors into transportation markets, thus extending the range and decreasing the refueling time of electric vehicles. However, hydrogen production must achieve costs of less than \$2/kg to be competitive with incumbent technologies.[2] The HyS cycle is expected to achieve this cost target if paired with heat from a concentrated solar power plant or from an advanced nuclear (Gen-IV) reactor.[3]

The HyS process consists of three operations coupled in a continuous loop: SDE of water (making hydrogen product and sulfuric acid intermediate from recycled SO_2/H_2O and water feed), thermally driven decomposition of sulfuric acid (into SO_2, water, and oxygen), and separation of oxygen (removed as a co-product of the cycle) from SO_2/H_2O (for electrolysis). The current work focuses on improvements in the SDE process, as it is one of the major operations that impact the overall HyS cycle efficiency. Literature-reported results to date are far from the performance goals[4-6] (600 mV at 500 mA/cm^2 and 65 wt% sulfuric acid) set by technoeconomic analysis to meet the cost target.[7] From the literature, it is apparent that to meet the current, potential, and acid concentration goals simultaneously, operation must take place at high pressures and temperatures.[8] However, the harsh chemistry of the SDE limits the range of system component materials that can withstand the target operating conditions. In this work, low-loading precious metal electrodes prepared using easy-to-scale roll-to-roll techniques on two different PTMs were evaluated in MEAs. The effect of PTM pore structure was found to have a profound influence on the SDE performance. PTMs with an open pore structure exhibited higher current densities under the tested conditions. Furthermore, the SDE performance was evaluated at high pressures and temperatures and for the first time electrolysis potentials < 700 mV at 500 mA/cm^2 and sulfuric acid concentrations ~60% were achieved. These results show the narrowing of the gap between experimental results and performance goals.

Materials and methods

The materials used for the present investigation are given in the Supporting Information. SDAPP membrane was prepared following procedures previously reported.[9] Reversible cell potential, ohmic and kinetic overpotentials were calculated and measured according to published reports.[5] All overpotential calculations were performed assuming 100 % Faradaic efficiency for hydrogen and sulfuric acid production.

MEA fabrication

The Pt/C catalyst layers were coated directly onto the carbon paper PTMs using gravure or slot die coating in a similar manner to past work.[10, 11] For all coatings, the ionomer-to-carbon mass ratio was 0.9 (I/C) and the water:1-propanol mass ratio in the catalyst ink was 3:1. Gravure coating was used to prepare catalyst layers with average Pt loadings of 0.12 mg/cm^2 and slot die coating was used to prepare catalyst layers with Pt loadings of 0.32 mg/cm^2. Catalyst loading variance was less than 10% as measured using X-ray fluorescence spectroscopy. Details of electrode fabrication and MEA preparation are described in the Supporting Information.

Electrolyzer operation

The procedures for measuring the cyclic voltammetry and cell break-in have been previously reported.[5] After break-in, the cell was held at 0.95 V and with a fixed SO_2 flow (24 sccm; 1.4 stoichiometric ratio at 500 mA/cm^2). The cell was operated with 0.29 mL min^{-1} water fed to the cathode and without water fed to the anode. Once stable conditions were achieved at 0.95 V, a constant current of 500 mA/cm^2 was applied, and the back pressure of both the cathode and anode was increased to 103.4 kPa$_{gauge}$ by adjusting the back pressure regulator at the anode and cathode outlets. Further details about the setup can be found in the Supporting Information and in previous work.[5]

Optical Profilometry

Optical profilometry of the two carbon substrates was obtained using the Keyence VR-3000 Wide Area 3D Measurement System. Images were taken at 160x magnification. Image processing included tilt and shape correction.

Results and discussion

It is known that the product acid concentration has an important effect on the electrochemical performance of SDE production of sulfuric acid and hydrogen.[8] While Pt kinetics are generally not influenced by the acid concentration,[6] the ohmic overpotential increases due to the loss of hydration in the membrane.[5] However, one important effect of acid accumulation at the catalyst layer is its influence on the thermodynamic potential of the SDE reaction. Inefficient acid removal results in an increase in the local acid concentration, which is reflected as an increase in the open circuit potential and thus an overall increase in cell potential. According to our previous study, at a cell temperature of 105 ºC and atmospheric pressure, having an acid concentration change from 35 wt% to 60 wt% results in an increase of 104 mV in thermodynamic potential (from 0.254 V to 0.358 V, respectively).[5] With a performance goal of 600 mV at 500 mA/cm^2 while producing 60 wt% sulfuric acid,[7] minimizing all overpotentials becomes critically important. Localized retention of product acid at the catalyst layer can result in a localized increase in acid concentration. Various strategies can be implemented to minimize the localized acid concentration. Such a strategy was demonstrated by Colón-Mercado et al.,[5] where cell operation with water feed to the cathode side lowered the local acid concentration at the anode catalyst layer when a membrane having high water permeability was used. High performance electrodes (with high catalyst utilization and low mass transport) can further benefit from improved acid removal from the porosity and morphology of the PTM that supports the catalyst layer. Therefore, PTMs supporting the catalyst layer must be evaluated under flooded conditions such as those of the SDE. Gas diffusion electrodes (GDEs) with low-precious metal loading previously optimized for gaseous operation of low-platinum group metal proton exchange membrane fuel cells were used to study the influence of two commonly used PTMs on the SDE performance.[10]

The GDEs evaluated in the present study were prepared by gravure coating the catalyst layer on SGL 29BC and Freudenberg H23C8 PTMs with a Pt loading of 0.12 mg/cm^2 and an I/C ratio of 0.9. The performance was evaluated using N115 membrane at 95 ºC after subjecting the cell to break-in conditions described in the Supporting Information. The effect of different PTMs on the electrolyzer performance is clearly shown in Figure 1a. The electrode that uses SGL 29BC as the PTM exhibits superior electrochemical performance compared to the electrode that uses Freudenberg H23C8. Because both electrodes were tested under identical conditions using the same membrane and catalyst layer fabrication conditions, other factors that influence the electrochemical performance, such as the Pt electrochemical surface area (ECSA), were considered. Figure 1b shows the cyclic voltammetry of the two Pt electrodes employed in the SDE cell. As observed in the figure, the ECSA is practically identical for the two electrodes, suggesting that the reason for the difference in performance is not due to catalyst layer properties and is attributed to the mass transport limitations arising from the carbon paper PTM itself. As reported in our previous study, thermodynamic equilibrium potential of the electrolyzer is severely affected by the acid concentration; therefore, any trapped acid will negatively influence the cell performance.[5]

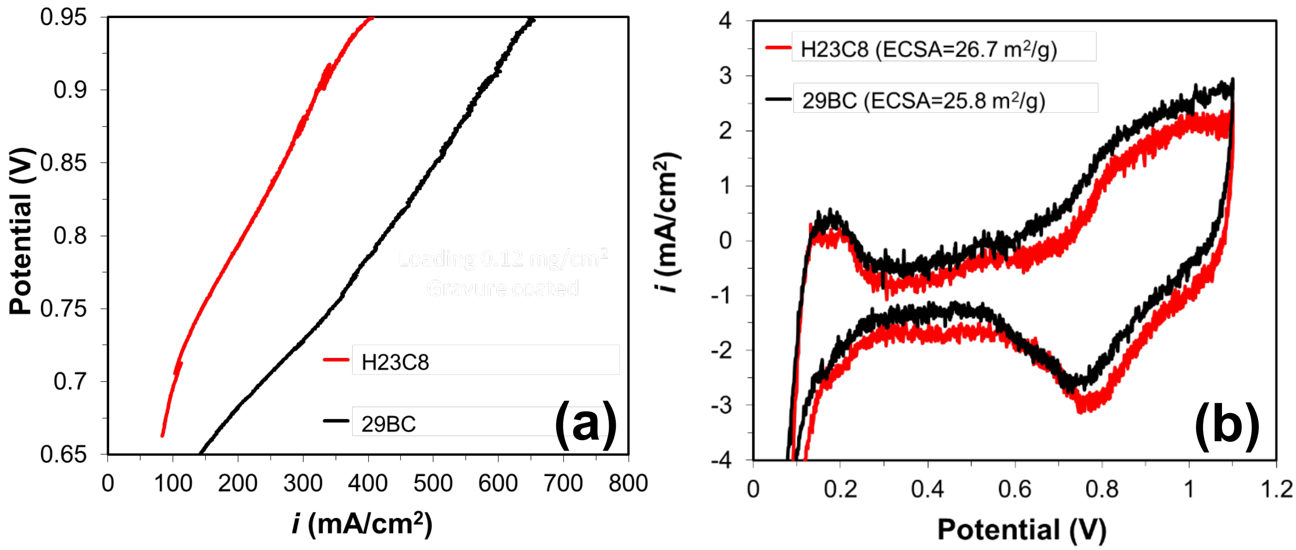

Figure 1. a) Electrolyzer performance of Gravure coated water rich ink on SGL 29BC and Freudenberg H23C8 PTM. Test performed using break-in conditions of 95 ºC using N115 with symmetrical anode and cathode electrodes having catalyst loadings of 0.12 mg$_{Pt}$/cm^2. b) Cyclic voltammetry and electrochemical active surface area for the electrodes tested using SGL 29BC and Freudenberg H23C8 PTM.

Figure 2 shows the optical profilometry of the flow-field facing side of the SGL 29BC and Freudenberg H23C8 PTMs. While both PTMs are similar in thickness (~215µm), their structure varies due to the use of different materials and different manufacturing methods. The Freudenberg H23C8 PTM has thin fibers that form a close-knit matrix (Fig. 2a), which results in small pore formation due to the densely packed thin fiber arrangement (Fig. 2c). On the other hand, the SGL 29BC PTM has thicker fibers that form a more open structure (Fig. 2b), resulting in a more open pore structure from the loosely packed thick fiber matrix (Fig. 2d). These results agree well with our qualitative observations from published works where high SDE performance was obtained using open porosity carbon cloth- and carbon paper-based electrodes.[5, 6, 12, 13]

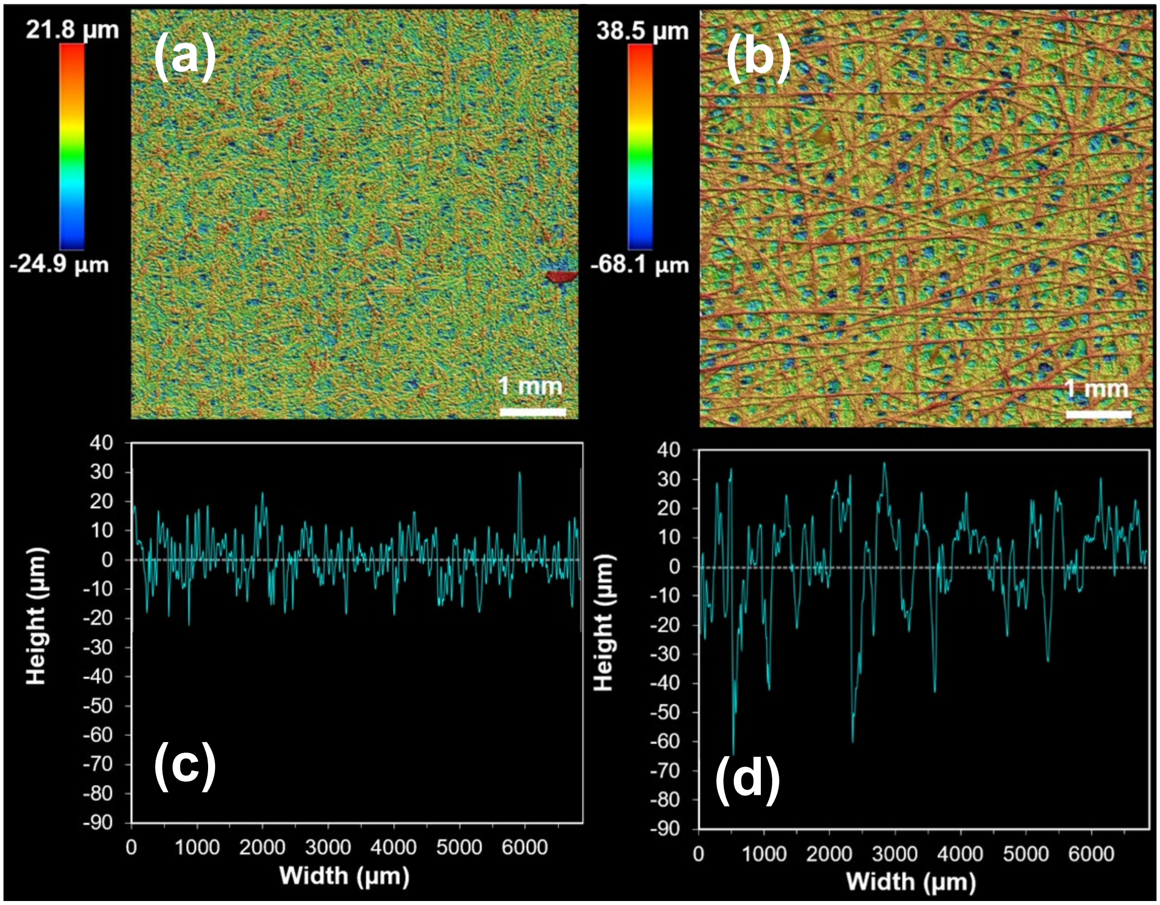

Figure 2. Optical profilometry results obtained for the back side of the two carbon paper substrates: (a,c) Freudenberg H23C8 and (b,d) SGL 29BC. Images (a,b) show the 3D height maps and (c,d) show the surface profile graph.

An attempt was made to further increase the SDE performance by increasing the catalyst loading (lower kinetic overpotential) and using thinner membrane (lower ohmic drop and higher water transport). Figure 3 shows the performance of SGL 29BC GDE with a loading of 0.321 mg/cm^2 (prepared by slot die coating) with two different 50 μm thick membrane materials. Data points shown for comparison in Figure 3 were obtained for the cloth based GDEs using N212 and SDAPP membranes from a previous study.[5] Since the electrode material employed is the same for both cells, the ECSAs are similar for both MEAs. As previously reported, the performance is much higher when using the SDAPP membrane due to its higher water transport and lower ionic resistance. The observed performance for the MEA with SDAPP membrane shows similar values at low current densities for the carbon paper GDE and previously reported carbon cloth electrode even though the catalyst loading on SGL 29BC in the present study is 36 % lower than the one reported previously. This result indicates that this level of catalyst loading reduction does not affect the electrolyzer performance. However, at high current densities, the performance of the carbon paper starts to deviate from that of the carbon cloth electrodes as there is an increase in mass transport limitations for the carbon paper based GDE as compared to the cloth based GDE. This result substantiates the conclusions drawn from Figures 1 and 2 regarding the effect of the PTM on mass transport limitations due to acid retention in the catalyst layer and insufficient product removal. However, even with the use of a membrane having high hydration, the SDE performance at the tested conditions is far from the performance goals.

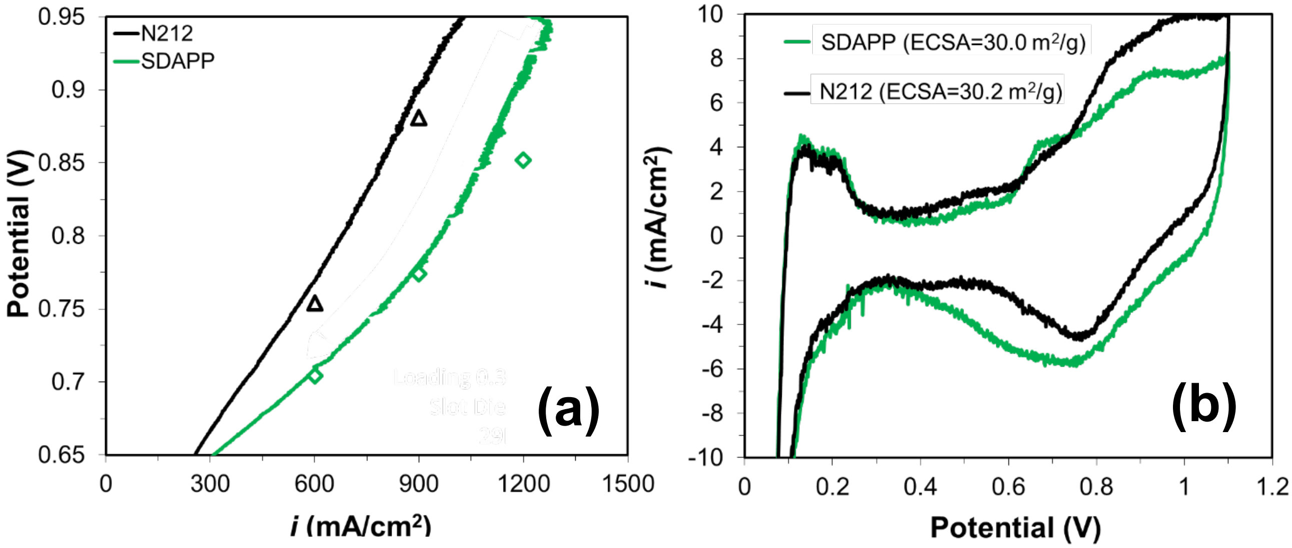

Figure 3. a) Electrolyzer performance of slot die coated water rich ink on SGL 29BC PTMs. Test performed using break-in conditions at 95 ºC using N212 and SDAPP with symmetrical anode and cathode electrodes having catalyst loadings of 0.321 mg_{Pt}/cm^2. Data points from previously published data using cloth based GDE with 0.5 mg_{Pt}/cm^2 are shown for comparison purposes.[5] b) Cyclic voltammetry and electrochemical active surface area for the electrodes tested using SGL 29BC PTM.

Maximizing the electrolyzer performance requires the SDE to be operated at high temperatures and pressures while maintaining high water availability in the MEA to facilitate lower ohmic losses and to achieve low kinetic and mass-transport limitations. Figure 4 shows the results obtained from the electrolysis cells tested at 103.4 kPa_{gauge} and operating temperatures between 110 ºC and 130 ºC. At atmospheric operating conditions, previously reported stable performance[5] was achieved at a maximum temperature of 105 ºC; however, under pressurized conditions, the electrolysis performance could be evaluated up to 130 ºC. The improvements observed from the high temperature operation were reflected in lower kinetic and ohmic overpotentials. These improvements counter the increase in thermodynamic potential due to the increase in acid concentration and system temperature.[14] For both MEAs, the lowest cell potential was obtained at 125 ºC. Increasing the MEA operating temperature from 105 ºC to 125 ºC (0 kPa_{gauge} to 103.4 kPa_{gauge}, respectively) results in a combined kinetic and ohmic overpotential reduction of 66 and 88 mV for SDAPP and N212 membranes, respectively. Further increase in temperature, while it appears to progressively lower the ohmic and kinetic overpotentials, results in an overall increase in cell potential due to the rapid increase in acid concentration and hence the thermodynamic potential. These results indicate that to improve the overall SDE performance, more active electrocatalysts are needed to lower the kinetic overpotential and thus lower the cell potential.

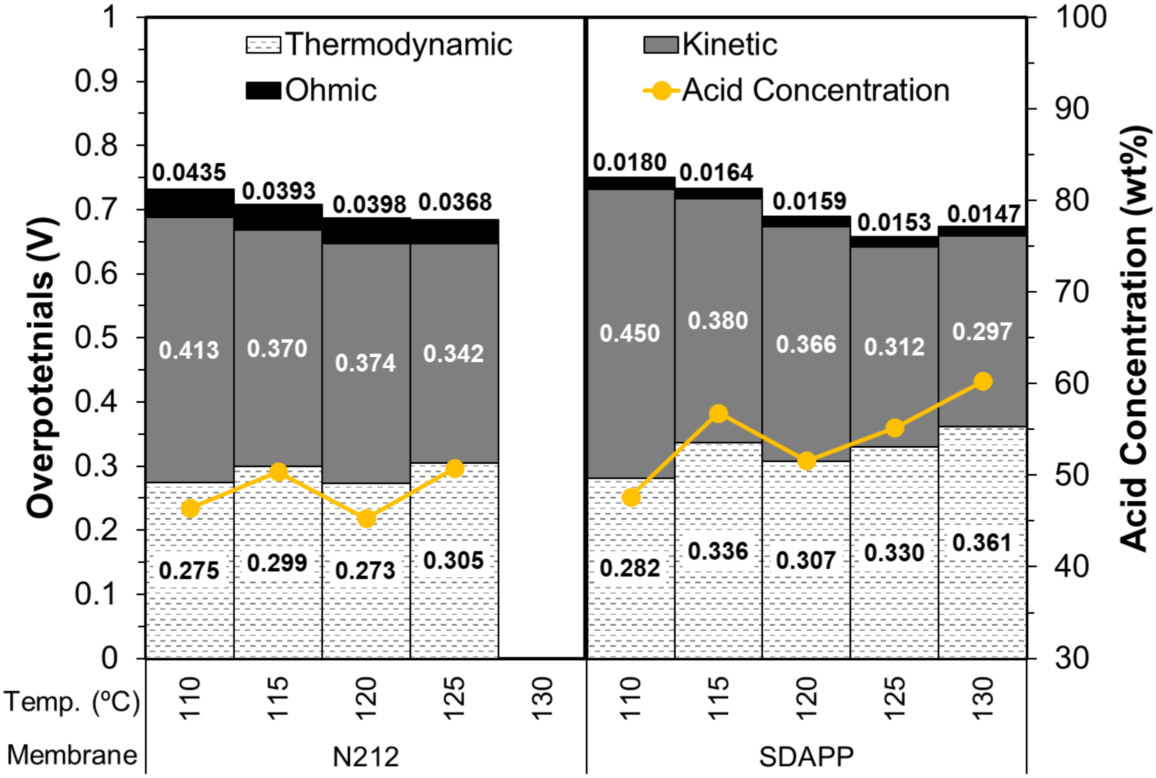

Figure 4. Electrolyzer results for MEAs utilizing N212 and SDAPP membranes and symmetrical anode and cathode electrodes having catalyst loadings of 0.321 mg_{Pt}/cm^2operated at 500 mA/cm^2 with constant water flow at the cathode and dry SO_2 and 103.4 kPa_{gauge} as a function of temperature. The sum of the overpotentials corresponds to the total cell voltage. Acid concentration is represented by the line for the different operating conditions taking into consideration water crossover from the cathode and the operating conditions of cell temperature and pressure. Numerical values are given to the individual overpotential.

Conclusions

The influence of PTMs on the GDE performance was studied by comparing the performance of two commercial carbon papers for SDE operation. Results indicate that the SDE performance benefits from an open structure such as that of carbon cloth and SGL 29BC. The result is indicative of effective product acid removal from the catalyst layer which drives the reaction towards higher efficiency. Employing optimized catalyst layers on roll-to-roll prepared GDEs on SGL 29BC in combination with thin membranes, and optimized operating conditions allows for efficient SDE operation. High pressures and high temperatures allow the production of high acid concentration (>60 wt%) while maintaining cell potentials below 700 mV at 500 mA/cm^2. High temperature and high pressure also resulted in low ohmic and kinetic overpotentials while allowing the production of high acid concentration. The overall SDE performance resulted in lower component overpotentials that counter the thermodynamic voltage increase due to high product acid concentration and high temperature operation. Further improvements could be attained by lowering the kinetic overpotential through the development of more active anode electrocatalysts.

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