Diagnosis and Modeling of the CuCl electrolyzer using Electrochemical Impedance Spectroscopy

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The CuCl thermochemical cycle, a novel H_2 producing technology, has been studied because of the moderate temperature requirements and high efficiency [1, 2]. Significant improvement in voltage and current efficiencies of the CuCl electrolyzer, a key component of the cycle, was recently obtained in our laboratory at Penn State [3-5]. A part of this project was focused on modeling the CuCl electrolyzer using electrochemical impedance spectroscopy (EIS) and understanding the system response as a function of temperature.

The CuCl electrolyzer was operated with 2 mol L^{-1} CuCl (aq) and 7 mol L^{-1} HCl (aq) as anolyte, and 7 mol L^{-1} HCl (aq) as catholyte. Nafion 117 polymer membrane was used to fabricate the MEA and 0.8 mg cm^{-2} Pt loading was applied on each side. The electrolyzer was operated at different temperatures, and Figure 1 shows the system behavior at 30 and 80 ºC. EIS was used to characterize the cell performance and the AC data was taken in the frequency range of 10 mHz to 50 kHz. The corresponding polarization curves (Figure 2) were also collected to correlate the AC and DC data.

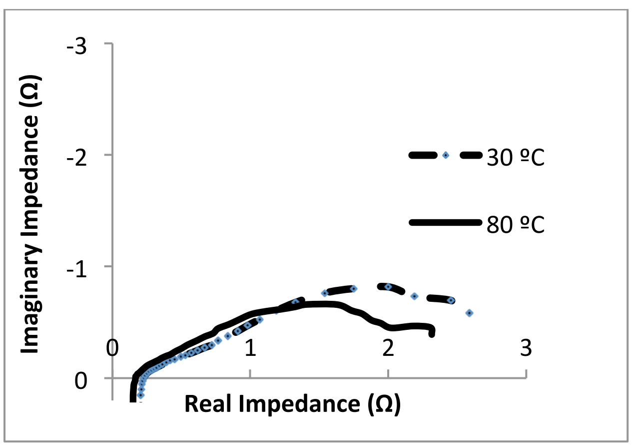

Fig. 1. EIS data obtained for the CuCl electrolyzer at 30 and 80 ºC.

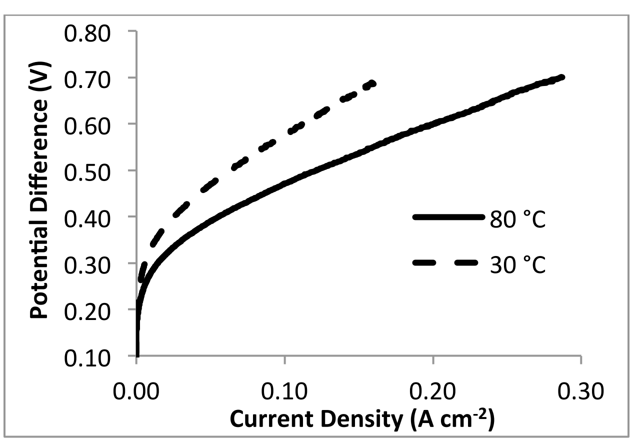

Fig. 2. Polarization curves obtained for the CuCl electrolyzer at 30 and 80 ºC.

An equivalent circuit model for the CuCl electrolytic cell was proposed as shown in Figure 3. The model consists of the membrane ohmic resistance (R_{ohm}), the charge transfer resistance (R_{ct}), and the mass transfer resistance (R_m). The constant phase elements (CPEs) were used to fit the relaxation time of each process. The model accurately fitted the experimental data, and Kramers-Kronig transformations were used to check for internal consistency before any further analysis was performed.

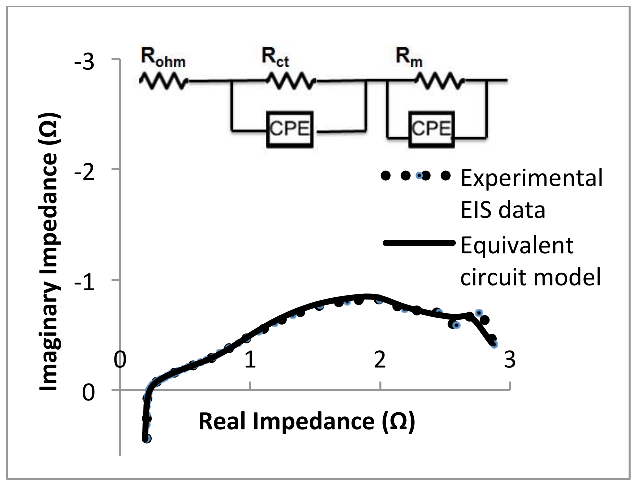

Fig. 3. Nyquist plot for the CuCl electrolyzer with the corresponding equivalent circuit model.

In addition, the circuit components shown in Figure 3 were used to simulate the EIS data and to quantify the contributions of different processes affecting the system performance. It was found that the membrane resistance decreased with increasing temperature, and it was observed that the conductivity estimated from EIS for the electrolyzer was similar to the value obtained using a single through-plane conductivity cell. Further, the calculated EIS parameters were fitted in the modified Butler-Volmer equation and a good correspondence was made between the AC and DC data. The model shows the percentage increase in the charge transfer rate and conductivity with temperature. The obtained electrochemical characteristics and modeling results will be used to better understand the behavior of the electrolyzer over a wide range of temperatures.

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References:

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