Title: Experimental Investigation of CO_2 Loss in a Membrane Electrode Assembly-Anion Exchange Membrane Cell.

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Highlights

- The elemental carbon balance in the cathodic compartment of the Membrane Electrode Assembly-Anion Exchange Membrane cell was quantified in this study by using the chronopotentiometry technique, gas chromatograph and mass flowrate readings.
- A direct correlation was observed between the loss of CO_2 into side reactions and the generation of CO, indicating that (bi)carbonate ion (HCO_3^- /CO_3^{2-}) are likely the main side reaction products.
- The loss of CO_2 remained consistent while the hydrogen evolution reaction (HER) dominated, implying a distinct reaction mechanism for CO_2 loss during electrochemical CO_2 reduction reaction (ECO2RR) and HER under a CO_2 atmosphere.

1. Introduction

A Membrane Electrode Assembly-Anion Exchange Membrane cell shows promising commercialized potential in the electrochemical CO_2 reduction reaction technique. A critical challenge that has been identified is the CO_2 cross-over phenomenon [1], where a portion of the inlet CO_2 reacts with hydroxide generated from both ECO2RR and HER ($CO_2 + OH^- \leftrightarrow HCO_3^- + OH^- \leftrightarrow CO_3^{2-}$). It not only consumes the reactant (CO_2), resulting in a lower energy efficiency but also highly risks the precipitation of (bi)carbonate salts on the electrode, thereby reducing the cell durability [2]. Thus, this phenomenon requires thorough examination.

In this study, the elemental carbon balance was quantified in the cathodic compartment of an MEA-AEM cell with a porous silver electrode. It reveals the correlation between the loss of CO_2 into side reactions and the production of CO and H_2, which offers insight into the reaction mechanism of the CO_2 cross-over phenomenon and benefits for optimizing the cell design and operation.

2. Methods

The elemental carbon balance is formulated as follows:

$$CO_{2\ Inlet} = CO_{2\ Unreacted} + CO_{\ Produced} + CO_{2\ Loss\ to\ side\ reactions}$$

To determine the proportion of CO_2 loss into side reactions, accurate measurement of the $CO_{2\ Inlet}$, the CO produced and the unreacted CO_2 during the ECO2RR is crucial. A Membrane Electrode Assembly-Anion Exchange Membrane cell is employed to conduct the ECO2RR under ambient conditions with an electrolyte of 0.1 M $KHCO_3$. The relationship between CO_2 loss and the generation of CO and H_2 is investigated by the chronopotentiometry technique. The assessment covers two scenarios: First, with an applied current density ranging from -25 mA/cm^2 to -125 mA/cm^2, representing the low current density region where ECO2RR dominates; Second, with an applied current density ranging from -450 mA/cm^2 to -600 mA/cm^2, where the HER prevails.

Before initiating the chronopotentiometry experiment, the inlet CO_2 is measured by gas chromatography when the cell is not under any electrical input. Subsequently, during the chronopotentiometry test, the gaseous effluent from the cathodic compartment of the cell is directed to the mass flow meter and gas chromatograph for online identification and quantification of gaseous products. This approach allows for the accurate quantification of inlet CO_2, unreacted CO_2, H_2 and CO produced, per unit time from the reactor.
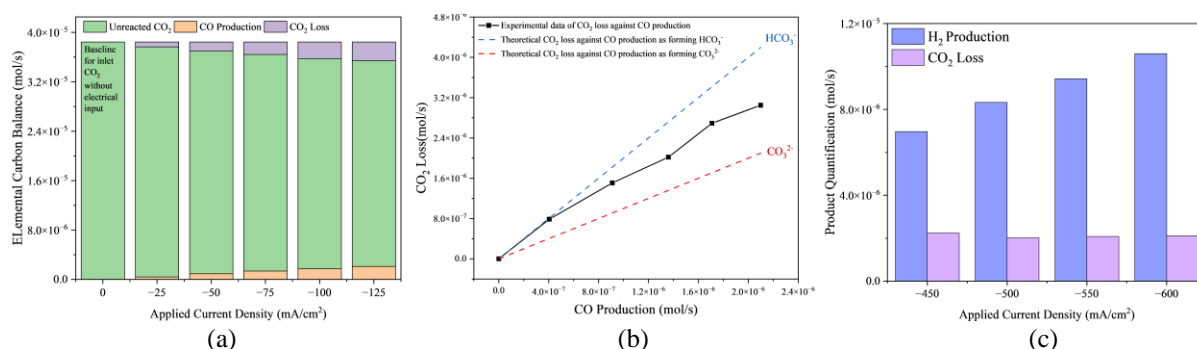
3. Results and Discussion

Figure 1: (a) Elemental carbon balance plotted against applied current density during the chronopotentiometry test for ECO2RR. Experimental conditions include a 0.1 M KHCO₃ electrolyte with a circulating flow rate of 8.2 ml/min and inlet CO₂ flow rate of 58 ml/min under ambient conditions (~20°C ± 2). (b) CO₂ loss as a function of CO production, derived from the data presented in Figure 1(a). The black solid line represents experimental CO₂ loss against CO production; the blue dashed line indicates the theoretical CO₂ loss against CO production, considering bicarbonate formation; the red dashed line presents the theoretical CO₂ loss against CO production, considering carbonate formation. (c) Bar chart illustrating the relationship between H₂ production and CO₂ loss with high applied current densities during the chronopotentiometry test for ECO2RR. Experimental conditions are the same as in Figure 1(a).

Figure 1(a) presents the elemental carbon balance quantification during the chronopotentiometry measurement. Figure 1(b) shows a direct correlation between the CO_2 loss and CO production. This suggests a hypothesis that the reactions forming the (bi)carbonate ion are likely the main competitive processes in the electrochemical reduction of CO_2, as the proposed reaction is $CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^-$, followed by $CO_2 + OH^- \leftrightarrow HCO_3^- + OH^- \leftrightarrow CO_3^{2-}$, resulting in the loss of CO_2 into (bi)carbonate per CO produced. The reaction mechanism for CO_2 loss appears to be dependent on the concentration of the hydroxide. However, Figure 1(c) illustrates that the CO_2 loss remains consistent at around 2.0 $\times10^{-6}$ mol/s while the HER ($2H_2O + 2e^- \rightarrow H_2 + 2OH^-$) prevailed at higher current densities from -450 mA/cm^2 to -600 mA/cm^2, aligning with observations from Haspel and Gascon [3]. It indicates a distinct reaction mechanism for CO_2 loss during ECO2RR and HER under a CO_2 atmosphere. This premise is elaborated upon in our full submission.

4. Conclusions

This work quantified the elemental carbon balance in the cathodic compartment of a Membrane Electrode Assembly-Anion Exchange Membrane cell with a porous silver electrode. Further data analysis suggests a hypothesis that the reactions forming the (bi)carbonate ion are likely the main competitive process in the electrochemical reduction of CO_2 at the low applied current densities. Also, the loss of CO_2 plateaus at the high applied current densities while HER, indicating the different environment for the hydroxide formed from ECO2RR and HER under a CO_2 atmosphere.

Reference

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[2] Sassenburg, M., Kelly, M., Subramanian, S., Smith, W. A., & Burdyny, T. 2022. Zero-Gap Electrochemical CO2 Reduction Cells: Challenges and Operational Strategies for Prevention of Salt Precipitation. ACS Energy Letters, 8(1): 321–331.
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