CH_4

Electrochemical CO_2 Reduction for Syngas Production

List of abbreviations

CO_2RR	CO_2 Reduction Reaction
FE	Faradaic Efficiency
GDL	Gas Diffusion Layer
MEA	Membrane-Electrode Assembly
MS	Mass-Spectroscopy
PBI	Polybenzimidazole
PEM	Proton-Exchange Membrane

Scope of project

The electrical power produced by renewable energies can be chemically stored as hydrogen and other fuels via electrolysis. CO_2 together with H_2O can be used in this context as a feed in order to produce valuable chemical products, such as CO, CH_4, C_2H_4, $HCOO^-$, or CH_3OH. This process will not only allow storing excess energy but also to close the CO_2 cycle, i.e., recycling of this greenhouse gas. The main challenges of the CO_2 reduction reaction (CO_2RR) are related to reduce its overpotential, increasing overall faradaic efficiency and better control product selectivity. Different aspects are studied at PSI's Electrochemistry Laboratory:

- development of analytical tools for online and operando detection of reaction products in the electrochemical reduction of CO_2;
- definition of the origin of selectivity for specific electrode materials;
- design electrocatalyst systems with high selectivity in the CO_2 reduction towards valuable products such as syngas, methanol or methane;
- development of polymer electrolyte based electrochemical cell.

In this report the focus is made on the development of polymer electrolyte electrochemical cells.

Status of project and main scientific results of workgroups

Importance of cell level development and short economic analysis

CO_2RR kinetics and products identification and quantification are mostly studied in half cell configurations using liquid electrolytes. This fundamental approach of studying CO_2RR is limited by the low solubility of CO_2 in water, the maximum CO_2 reduction current being in the range of 0.01–0.02 A/cm². In order to overcome the solubility problem and to reach higher operating current densities, CO_2 reduction needs to be carried out in a co-electrolysis system where pure or diluted gaseous CO_2 is used. To make a co-electrolysis system economical feasible, efforts have to be concentrated on design of highly efficient cells, development of catalysts and their incorporation into an efficient co-electrolyser designed for high-current-density operation.

A recent economic analysis from our group has identi-fied that the electrochemical production of CO and formate from CO_2 shows the most promising perspective [1]. CO production costs ranging from 0.27 to 0.48 \$/kg are below the current market price of 0.65 \$/kg. CO in combination with H_2 (syngas) serves as an important chemical precursor for a significant number of industrial processes (e.g. Fischer-Tropsch synthesis). Another interesting product of CO_2RR is formic acid. The estimated production cost for this product is a factor of 2–4 below the current market price for formate/formic acid (0.34 vs. 0.8–1.2 \$/kg). The analysis is based on an operating current density of 0.2 A/cm² and the same electrolyzer capital cost as for commercial alkaline water electrolyzers.

Based on this economic study, at this stage of the project, the studies are focused on CO production. The catalytic materials selective for CO production from CO_2 are Ag, Au and Zn [2]. Gold was selected as a benchmark catalyst for these studies since it can be used in different pH ranges without major chemical stability issues.

In our cell development, we chose an approach using gas diffusion electrodes allowing to reduce mass transport losses related to the relative low solubility of CO_2 in water under ambient conditions (ca. 0.033 mol/L) and enabling the cell to operate at high current densities, similar as it is used for membrane water electrolysis systems.

Experimental

The electrochemical cell and the experimental setup are similar to that used for fuel cell studies [3]. Two membrane-electrode assembly (MEAs surface 1 cm²) configurations were tested. The first one consists in an electrochemical cell with a proton exchange membrane as unique core electrolyte and the second consists in a modified electrochemical cell with a pH-buffer layer of aqueous $KHCO_3$ between the cath-

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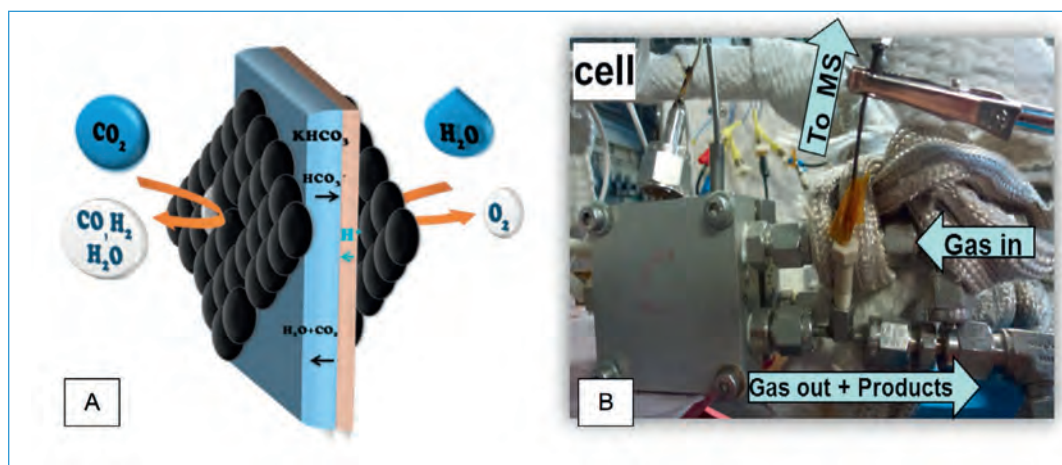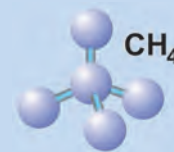
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ode catalyst and the proton exchange membrane. A schematic representation of the modified electrochemical cell is given in Figure 1 A. The proton exchange membrane used was a Nafion® XL 100 and the buffer layer was composed of an aqueous electrolyte supported in glass fibres (Whatmann® paper GF/D, 2.7 µm pore size).

Regardless of the cell design, the catalyst used at the cathode side was gold black (Sigma Aldrich) spray coated on a carbon gas diffusion layer (SGL 24 BC). At the anode side spray coated Pt/C (47 % wt. Pt on carbon TEC10E50E TKK) on gas diffusion layer (GDL) was used with a loading of 0.4 mg_{Pt}/cm^2.

The cathode was operated using nitrogen (electrolysis mode) or using carbon dioxide (co-electrolysis mode). At the anode side pure hydrogen gas was used and this electrode was employed as a reference electrode for the system ($U_{anode} = 0$ V vs RHE at pH 0). The outlet of the cathode compartment was connected to a mass spectrometer in order to identify the CO_2RR products (the experimental setup used in this study is shown in Figure 1 B). In all measurements the cathode flow was set to 10 mL/min, whereas at the anode side the hydrogen flow was set to 50 mL/min. The cell was operated at 40 °C, under full humidification conditions and ambient pressure. The polarization curves were measured galvanostatically. For each data point, the cell current was stabilized for 2 minutes before measurement.

## Results and discussion

PEM configuration

When MEAs based on the proton-exchange membrane (PEM) was used and fed with CO_2 no gaseous CO_2-reduction products were detected by mass-spectroscopy. This result is in agreement with another study reported in the literature [4] and shows that this cell configuration is not suitable for co-electrolysis systems under the test conditions used here. The acidity of the membrane shifts the cathode selectivity to hydrogen evolution. Hence, for operation in co-electrolysis mode, the pH value of the cathode needs to be modified.

Modified PEM configuration – Proof of principle

A cell with a buffer layer (aqueous 0.5 M $KHCO_3$ solution imbibed in glass fiber) was used for CO_2 reduction. The iR polarization curves are shown in Figure 2 and the results are compared to available literature data with good agreement. One of the targets could be readily achieved, namely the co-electrolyzer operation at current densities > 0.2 A/cm^2. The CO_2 reduction products were detected by mass-spectroscopy (MS).

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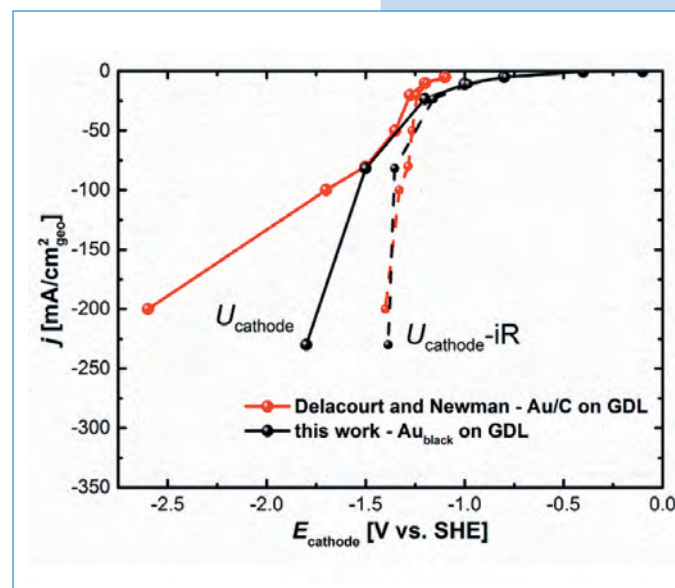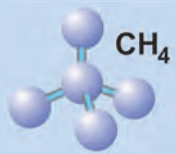
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As illustrated in Figure 3, the reduction of CO₂ resulted in the expected evolution of H₂ (m/z = 2) and consumption of CO₂ (m/z = 44), along with an increase in m/z = 28 that points at the production of carbon monoxide. The faradaic efficiency (FE) for CO production calculated from the mass spectrometer signal was aprox. 10 %. A first approach to increase the CO faradaic efficiency is related to the way of engineering the electrodes.

More efforts are needed in this domain. Several directions are proposed for the next time frame and they are going to be realized in collaboration with other groups involved in the project:

- increasing the gold active site distribution on the GDL (reduce carbon content),
- synthesis of gold nanoparticles or
- substituting the GDL/catalyst layer structure with Au mesh.

However, these first results prove the setup feasibility developed in our laboratory during the first project year.

Outlook

Up to date, the buffer layer cell configuration is only a proof of concept. The cell stability being a major issue in this case, new stable buffer layers are needed. Exchange of the glass fiber based buffer layer with an intermediate layer of poly-benzimidazole (PBI) showed first improved results and will be further developed in the next steps.

Figure 3:

(A) Ion current recorded by MS for different mass fraction (m/z) and
(B) ion current ratio between mass fractions corresponding to CO₂ and CO proving the formation of carbon monoxide.
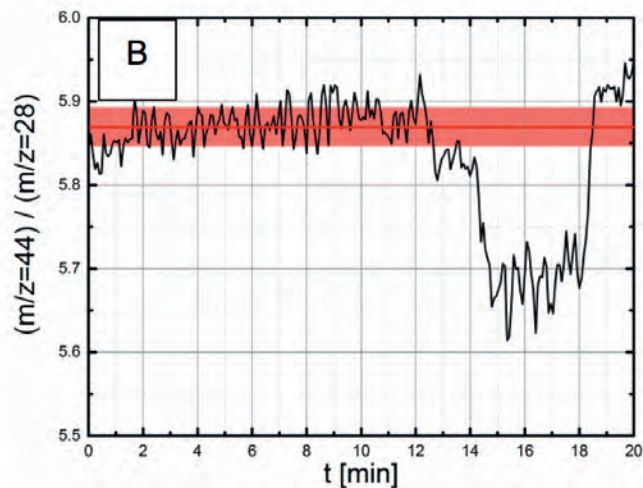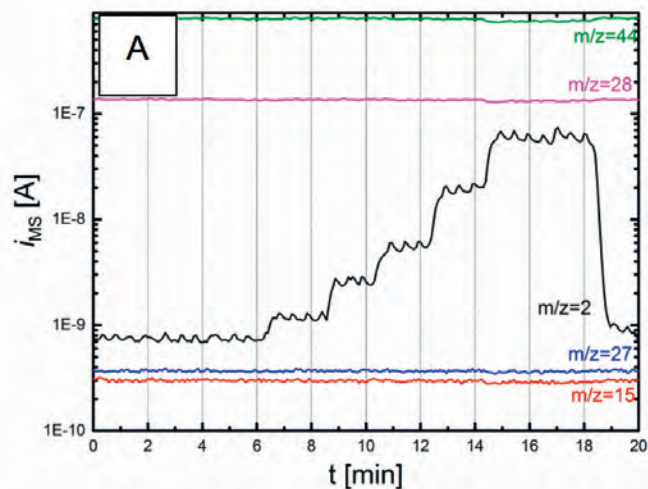
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