Design Principles of Bipolar Electrochemical Co-Electrolysis Cells for Efficient Reduction of Carbon Dioxide from Gas Phase at Low Temperature

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Cell designs for the electrochemical reduction of CO₂ from gas phase were developed and investigated, and the critical elements for an efficient process were identified. Various types of polymeric membrane were used to build membrane electrode assembly adapted for CO₂ reduction in gas phase: protonic and anion exchange membrane (AEM), bipolar membrane and a modified bipolar like membrane configuration. Configurations using anion exchange ionomer in the cathodic catalytic layer in contact with an AEM allow for a great enhancement of the cathode reaction selectivity toward CO₂. However, a severe problem was identified when co-electrolysis is performed using only an AEM: this type of membrane acts as a CO₂ “pump” meaning that for each molecule of CO₂ reduced at the cathode, one or two CO₂ molecules are produced at the anode by oxidation of the carbonate/bicarbonate anion transported in the membrane. A bipolar membrane system was shown to soften this problem, but only a newly developed cell design was able to fully prevent the parasitic CO₂ pumping. Using this new cell configuration, the faradaic efficiency of an alkaline environment is maintained, the parasitic CO₂ pumping to the anode side is completely suppressed, and the overall cell voltage efficiency is highly improved.© The Author(s) 2019. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.1221816jes]

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The electrochemical reduction of carbon dioxide is a very attractive proposition for minimizing the level of atmospheric CO₂, for reutilizing CO₂ emissions from fossil fuel sources, and for storing energy when it is coupled to a renewable energy source such as wind or solar PV. In this process, carbon dioxide is converted to fuels or chemical feedstock, which, depending on the process efficiency, could be generated at a competitive price when compared with chemicals that are conventionally derived from petroleum. Technically, CO₂ reduction can be carried out in an electrochemical co-electrolyzer device where two processes are coupled: CO₂ reduction at the cathode side and water oxidation at the anode side. For this purpose, not only cathode catalyst materials with favorable electrokinetix that contribute to CO₂ reduction are necessary, but also highly rational device engineering, taking into account the constraints of unwanted side reactions, is required in order to achieve high performance in CO₂ co-electrolysis.

The electrochemical CO₂ reduction reaction (CO₂RR) is a complex reaction which would preferably occurs with high reaction products selectivity and high energetic efficiency. The reaction selectivity is mainly determined by the type of catalyst and by the pH of the electrolyte/environment. Therefore, CO₂RR using a liquid electrolyte, either aqueous or organic, is being actively pursued in CO₂RR research. Using a liquid electrolyte, the pH can be easily controlled and the activity and selectivity of the CO₂RR on a specific catalyst surface can be investigated. However, the main drawback of this approach is related to the limited solubility of CO₂ in aqueous solutions (∼30 mM in H₂O at atmospheric pressure and room temperature) resulting in CO₂ transport-limited current densities not exceeding 30 mA/cm². In order to scale up the process, the current densities must be maximized and one way to achieve this is the direct use of CO₂ from the gas phase in a polymer electrolyte membrane cell configuration. Thus, gas phase electro-reduction of CO₂ represents a valuable opportunity to incorporate renewable energy into the chain of chemical industry.

Different types of electrochemical membrane reactors operating at low temperature have been presented for CO₂ reduction from gas phase. These designs can be classified into two major types: gas-liquid type and gas-polymer electrolyte or liquid-free type. In the gas-liquid type, the cathode is generally a gas diffusion electrode (GDE) and it is fed on the external side with gaseous CO₂. The two cell GDEs are separated by a flowing electrolyte and a ion conductive membrane. The membrane is used as a separator between the cathodic and the anodic compartment. In such a configuration, the pH is easily controlled by simply adding the suitable salt/acid/base to the liquid electrolyte. Current densities up to 120 mA/cm² at a cell voltage of ~4 V and high paraadaic efficiencies for formic acid using a RuPd cathode catalyst were reported using such a configuration.

In the liquid free type cell configuration, the cathode electrode is generally a GDE with the internal catalyst layer side in direct contact with the ion conductive membrane and the external side being fed with CO₂ gas. In such a configuration, the cathode pH environment is mainly determined by the ion conductive polymer (ionomer) of the electrolyte membrane and by the ionomer applied directly within the catalytic layer composition. Therefore, the choice of the polymer type, i.e. anion exchange polymer vs. cation exchange polymer, as well as the detailed architecture of the entire membrane electrode assembly (MEA) are crucial parameters for efficient liquid-free CO₂ reduction from gas phase. Up to now, few studies of CO₂ reduction in gas phase have been published, either using cation exchange membranes (CEM) or anion exchange membranes (AEM) or bipolar membranes (BM). When proton exchange membranes are used for CO₂ reduction co-electrolysis, the concomitant hydrogen evolution reaction (HER) is a major issue, because the acidity of the membrane shifts the cathode selectivity toward HER. Delacourt et al. have shown that, using a Nafion membrane for CO₂ reduction co-electrolysis, the only product detected at the cathode side is hydrogen. However, in other studies with similar systems, CO₂RR products were detected in variable quantities depending on the cathode catalyst used. The detailed results depend on the catalyst used and the operating conditions. The main advantage of this reactor design is related to the high voltage efficiency that can be reached. In order to improve the faradaic efficiency (FE) and the activity toward CO₂RR, the alkaline membranes has been used. Using alkaline conditions, improved CO₂ reduction selectivity was reported with faradaic efficiency values for different CO₂RR products ranging from 3% to 50%. However, due to ohmic resistance limitations of state-of-the-art alkaline exchange membranes, the energetic efficiency of such systems is decreased compared to those using proton exchange membranes.
Moreover, when such membranes are used, the transported ions in the membrane are OH\(^{-}\), HCO\(_3\)\(^{-}\) and CO\(_3\)\(^{2-}\) which are oxidized at the anode to produce O\(_2\) and CO\(_2\).\(^{23}\) A quantification of the CO\(_2\) produced at the anode is addressed in this study and the overall cell effectiveness is discussed when alkaline membrane is used. In the study where a bipolar membrane was used in a purely gas phase co-electrolyzer, no FE values were reported.\(^{15}\)

In the present work, two types of cell configurations are presented and investigated for technical CO\(_2\) reduction from gas phase which are based on a rational design approach taking into account a variety of subtle, but crucial details that appear to be ignored in previous cell designs. The first configuration utilizes a bipolar membrane with the anion conductive (alkaline) side of the bipolar membrane facing toward the cathode. In this way, the cathode pH can be maintained at high values desirable for efficient CO\(_2\) reduction. The cation conductive (acidic) side of the bipolar membrane, which faces the anode, prevents carbonate/bicarbonate species of the alkaline side to migrate to the anode and to be oxidized there to release CO\(_2\). This latter process represents a major loss channel for CO\(_2\) in an entirely alkaline membrane system. The bipolar cell configuration has been further improved in a second cell configuration presented in this work, which enables highly improved energetic efficiency.

In order to assess and compare the different cell configurations, we have chosen to study the electro-reduction of carbon dioxide to carbon monoxide on gold catalysts. It is well known that the reduction of CO\(_2\) to CO is relatively facile compared to the formation of other products like alcohols and alkanes. Nevertheless, CO in combination with simultaneously produced H\(_2\) can be used as syngas. Gold, together with Ag, Sn, and Zn, is a well-known catalyst selective for the production of CO and it was chosen in the present study for its chemical stability in a very broad range of pH.\(^{4,28,29}\) In this manner, the same catalyst could be applied in all different cell configurations investigated in this work.

**Experimental**

**Materials.**—Nanoparticulate pure Au “black” from Sigma Aldrich was used as cathode catalyst for CO\(_2\) reduction in all cell configurations presented here. IrO\(_2\)-TiO\(_2\) from Umicore and Pt/C 47 wt% catalyst from Tanaka (TEC10E50E) were used as anode catalysts for oxygen evolution reaction (OER) and for hydrogen oxidation reaction (HOR), respectively. Nafion XL 100 from DuPont was used as cation exchange membrane without pre-conditioning. The anion exchange membrane was Fumasep AA30 provided by Fumatech. For the preparation of this additional thin film, a Nafion ionomer. A schematic representation is shown in Figure 1. Moreover, when such membranes are used, the transported ions in the membrane are OH\(^{-}\), HCO\(_3\)\(^{-}\) and CO\(_3\)\(^{2-}\) which are oxidized at the anode to produce O\(_2\) and CO\(_2\).\(^{23}\) A quantification of the CO\(_2\) produced at the anode is addressed in this study and the overall cell effectiveness is discussed when alkaline membrane is used. In the study where a bipolar membrane was used in a purely gas phase co-electrolyzer, no FE values were reported.\(^{15}\)

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**Electrode preparation.**—Adapted inks were prepared for each type of catalyst used here. Water and isopropanol (80 to 20 wt% ratio) were used as solvents for the preparation of Pt/C and IrTiO\(_2\). When Au “black” ink was prepared only MilliQ water was used as a solvent. The ionomer content was fixed at 30 wt% with respect to the catalyst weight when Pt/C was used. For IrO\(_2\)-TiO\(_2\) and Au black electrodes the ionomer content was 10 wt%.\(^{30}\) Varying amounts of catalyst inks were spray coated on 0.5 cm\(^2\) gas diffusion layers (GDL) Sigracet 24 BC (SGI, Carbon) in order to obtain different catalyst loadings: \(~0.4 \text{ mg Pt/cm}^2\), \(~10 \text{ mg IrO}_2\text{-TiO}_2\text{/cm}^2\) and \(~3 \text{ mg Au/cm}^2\). The spray coating process was carried out at room temperature and the electrodes were dried using the spray air flow.

**Types of cell configuration.**—The cell configurations or MEAs investigated for CO\(_2\) co-electrolyzers can be divided into two categories: “standard configurations” inspired by fuel cell architectures and an additional innovative cell configuration optimally designed for the purpose of gas phase CO\(_2\) reduction, which will be called “novel configuration” in the following. All investigated cells had 0.5 cm\(^2\) active geometric area.

**Standard cell configurations.**—The MEAs consist of two electrodes (i.e. gas diffusion electrodes) and a polymer electrolyte membrane in-between. These MEAs were fixed between two metallic gold coated flow fields. The membrane was sandwiched between the electrodes inside the cell without hot pressing (due to the low resistance toward increased temperature of the anion exchange membrane and the associated ionomer). The different types of cell configuration investigated in the present study are summarized in Table 1.

When a bipolar membrane was used, the alkaline side of the membrane was facing the cathode and the acidic side was facing the anode.

**Novel cell configuration.**—A new type of co-electrolysis cell configuration was optimally designed to maintain a high pH value at the cathode, to block the parasitic CO\(_2\) transport to the anode and to improve the energetic efficiency of the overall process. This cell design consists of a cathode catalyst layer containing Au “black” and anion exchange ionomer (prepared as described in Electrode preparation). This cathode catalyst layer was further covered by an additional thin film of anion exchange ionomer which separated the cathode from a Nafion XL membrane. For the preparation of this additional thin film, 0.1 mL of 5 wt% anion exchange ionomer solution was sprayed on top of the cathode catalyst layer and subsequently dried in air. The anode catalyst layer was based on Pt/C or IrO\(_2\)-TiO\(_2\) catalyst mixed with Nafion ionomer. A schematic representation is shown in Figure 1.

**Electrochemical measurements.**—For measurements investigating solely the cathode half-cell reaction, the anode catalyst was Pt/C and it was fed with pure H\(_2\) at 50 mL/min. In this operation mode, the anode serves both as counter and reference electrode, corresponding to a pseudo-reversible hydrogen electrode (pseudo-RHE). Depending on the measurement, either pure CO\(_2\), or a mixture of 50/50 vol.% CO\(_2\) and Ar was fed to the cathode side at 50 mL/min, the latter mixture chosen for reasons discussed below. However, for comparison, cathodic polarization curves were recorded also under pure CO\(_2\) and N\(_2\) (1). Cathode and anode gas humidification was achieved by passing through a water-bubbling system, the temperature of which was set to yield 100% relative humidity (RH). The cells were operated at 40 °C and ambient pressure.

| Cell name | Cathode catalyst | Cathode ionomer | Membrane | Anode catalyst | Anode ionomer |
|-----------|------------------|-----------------|----------|----------------|---------------|
| “acidic”  | Au black         | Nafion          | Nafion XL 100 | Pt/C          | Nafion        |
| “alkaline”| Au black         | Fumon/Alkaline  | Fumasep AA30 | Pt/C or IrO\(_2\)-TiO\(_2\) | Fumon/Alkaline |
| “bipolar” | Au black         | Fumon/Alkaline  | Fumatech FBM | Pt/C or IrO\(_2\)-TiO\(_2\) | Nafion        |
| “novel configuration” | Au black + Additional layer of alkaline ionomer | Fumon/Alkaline | Nafion XL 100 | Pt/C or IrO\(_2\)-TiO\(_2\) | Nafion        |
Polarization curves were measured between 0.1 and −2 V vs RHE with potential scans at 50 mV/s using a Biologic V5 300 potentiostat. Full co-electrolysis cell operation was also tested using IrO2-TiO2 anode catalyst. Pure, humidified CO2 was fed to the cathode at 100 mL/min and Ar with 100% relative humidity was fed to the anode. The cells were operated at 40 °C and ambient pressure. In these measurements, polarization curves were recorded in galvanostatic mode. For each cell current value, the cell potential was first stabilized for 15 minutes and data was then averaged over the last 3 minutes.

Stability measurements.—Stability measurements were performed for the bipolar cell and for the “novel” cell configuration. The cathode potential and the CO selectivity were evaluated for 22 hours of operation at −50 mA/cm2 constant current density. The cells were operated at 40 °C, ambient pressure and 100% RH. The anode catalyst was Pt/C and was fed with pure H2 at 50 mL/min. The cathode was fed with a mixture of 50/50 vol.% CO2 and Ar at 5 mL/min. The cathode exhaust gases were analyzed on-line by mass spectrometry, cf. below. The 22 h of stability measurements were completed in two operation times. In the first step, the cells were continuously operated for 21 hours, then stopped, disassembled, and the cathode dried for 24 hours. Then, the same cell was reassembled and restarted, and the stability test was continued for 1 hour.

Gas analysis – mass spectrometry.—The gas analysis was performed using a mass spectrometer (MS), Omnistar from Pfeiffer. The MS was carefully calibrated to quantify the gases H2, CO, CO2, N2, and Ar in the exhaust gas mixture by using several different calibration gas mixtures. Details about this multi-gas calibration method can be found elsewhere.32 Being the dominant cathode reaction products on Au catalyst,33,34 only CO and H2 were monitored at the cathode side in addition to the background gases CO2, Ar, and N2, the latter resulting from minor external gas intrusion into the system. Taking into account minor presence of N2 in the MS analysis turned out to be crucial for the unambiguous detection of CO at the cathode side due to the interference of both gases at their dominant MS peak m/z = 28. Applying the multi-gas calibration method, it was possible to unambiguously distinguish the interfering gases CO2, CO, and N2. During MS analysis of the CO2 reduction products at the cathode side, the cell was continuously fed with a humidified mixture of 50/50% vol CO2/Ar at 5 mL/min and operated galvanostatically at constant current. This cathode gas composition was chosen in order to be able to convert the product gas composition resulting from MS analysis into product gas flows for each separate gas component. This was enabled by the use of Ar as inert background gas, which was neither consumed nor produced in the cell reaction, and, therefore, could serve as constant reference mass flow. Three different currents were applied to the cell and maintained for 15 min at each point. The maximum CO and H2 concentrations detected during this holding time of 15 min at each current density were used for the estimation of CO production.

The CO selectivity was used as a parameter to estimate the CO2RR efficiency as defined according to Equation 1:

$$\text{selectivity} = \frac{\text{CO mol} \%}{\text{CO mol} \% + \text{H}_2 \text{ mol} \%}$$  

The current (or faradaic) efficiency of a specific gas product k was determined according to Equation 2:

$$FE_k = \frac{n_k F (x_k / x_{Ar}) V_{Ar}}{I}$$

Here, nk is the number of electrons exchanged to produce one molecule of gas product k, F is the Faraday constant (F = 96485 C/mol), xk is the mol % fraction of the gas k in the exhaust gas mixture determined by MS, vAr is the known molar flow rate of the reference gas Ar in mol/s, xAr is the mol % fraction of the reference gas Ar in the exhaust gas mixture determined by MS, and I is the total current in A.

For cathode potentials higher than ~1 V vs RHE, the CO faradaic efficiencies could not be determined due to unreliable CO signals in the MS which was below the detection limit.

The products of the anode reaction were also analyzed by MS in full co-electrolysis cell configuration, i.e. using IrO2-TiO2 as anode catalyst for the oxygen evolution at the anode side. In this case, CO2 and O2 were the gas products of interest in the anode exhaust gas mixture.

Liquid phase measurements.—The CO2RR on the same Au black catalyst in a liquid environment was performed using a similar cell to the one described in Reference 35. The electrode used for characterization in the electrochemical cell was 1 cm2 and contained ~1 mg Au/cm2. The cell was separated into two compartments by an anion exchange membrane (Selemion AMV). The counter electrode was a platinum sheet (1 cm2). A 0.1 M CsHCO3 (Sigma-Aldrich, 99.99%) was used as electrolyte. MilliQ water with a resistivity of 18.2 MΩ cm was used for electrolyte preparation. The electrolyte pH was 6.8. CO2 was flowed through the cell cathode with a flow of 5 mL/min during the measurements.

Results and Discussion

Influence of ionomer/membrane pH on CO2RR.—The CO2RR reaction is pH dependent and in gas phase co-electrolysis systems, the reaction pH is defined by the type of polymer electrolyte like in similar electrochemical devices, e.g. fuel cells and electrolyzers.3 During co-electrolysis in presence of gaseous CO2, the following dominant reactions occur on Au catalyst at the cathode side:

$$\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{OH}^- + \text{CO}_2$$

$$\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$$

$$\text{H}_2 + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{OH}^-$$

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$$

In Equation 1, nE is the number of electrons transferred to produce one molecule of gas product k. F is the Faraday constant (F = 96485 C/mol), xk is the mol % fraction of the gas k in the exhaust gas mixture determined by MS, vAr is the known molar flow rate of the reference gas Ar in mol/s, xAr is the mol % fraction of the reference gas Ar in the exhaust gas mixture determined by MS, and I is the total current in A.
H2 faradaic efficiencies were calculated for each particular case using Equation 2. The total FE add up to values between 75 and 92% (results types of membranes had the same thickness of 30 µm contained the same type of ionomer as the membrane used. Both polymer, Fumasep FAA 30. In both cases, the cathode catalyst layer exchange polymer Nafion XL 100 and "alkaline" anion exchange contained within the cathode catalyst layer: "Acidic" proton/cation active polymers were applied, both as membrane type and as ionomer technology are presented in the literature with a focus on developing new types of alkaline membranes and incorporating specific ionomer or ionic liquid into the cathode catalyst layer.6 In a recent publication, Kutz et al. presented 98% CO selectivity at a current density of 100 mA/cm² and a full co-electrolysis cell voltage of 3V using Sustainion membrane and Ag cathode catalyst.24

Despite these very promising results, in none of these studies the parasitic CO2 pumping to the anode side was investigated. The parasitic CO2 pumping represents a major problem for the efficiency of CO2 utilization of such alkaline membrane systems and this is discuss in the following section.

Parasitic CO2 pumping effect of alkaline membrane configurations.—The mobile ions inside an “alkaline” anion exchange membrane (AEM) in the presence of CO2 are expected to be carbonate (CO32−) and bicarbonate (HCO3−) species rather than OH− hydroxide ions. This fact imposes a severe problem for the overall CO2 reduction process because it results in the pumping of CO2 from the cathode side to the anode side as described in the following. It is evident from Reactions 5 and 6 that all cathode reactions lead to the formation of OH− at the cathode in alkaline conditions. This is not only true for the actual CO2RR, but also for the concomitant hydrogen evolution reaction. In abundance of CO2, these OH− are transformed into (bi)carbonate anions according to Reactions 7 and 8.

\[
2\text{OH}^- + 2\text{CO}_2 \rightarrow 2\text{HCO}_3^- \quad [7]
\]

\[
2\text{OH}^- + 2\text{H}_2\text{CO}_3^- \rightarrow 2\text{CO}_3^{2-} + 2\text{H}_2\text{O} \quad [8]
\]

Due to the electrostatic field in the membrane during operation, the (bi)carbonate anions migrate to the anode side where they are oxidized into O2 and CO2 according to reactions 9 and 10:25

\[
2\text{H}_2\text{O}_2 \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- + 2\text{CO}_2 \quad \text{E}_{\text{eq}} = 0.765 \text{ V vs. SHE} \quad [9]
\]

\[
\text{CO}_3^{2-} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{e}^- + \text{CO}_2 \quad \text{E}_{\text{eq}} = 0.692 \text{ V vs. SHE} \quad [10]
\]
Considering the overall CO2 balance in the system reveals that for each (bi)carbonate or bicarbonate is the major anion species in the membrane. Pumped from the cathode side to the anode side, depending on whether (bi)carbonate to form water and CO2, c.f. Reactions 11 and 12. This hydrogen oxidation, which, in a subsequent chemical step, react with CO2 molecules are transported to the anode side in the form of carbonate/bicarbonate and released there again in the form of CO2. Furthermore, additional CO2 molecules are transported to the anode side due to concomitant cathodic hydrogen evolution and other cathodic side reactions. This parasitic “CO2 pumping” from cathode to anode side provides a huge loss channel for CO2 and, therefore, makes “alkaline” AEM co-electrolyzer systems intrinsically inefficient for the desired electrochemical reduction of CO2. The formation of CO2 at the anode side as a result of this CO2 pumping effect was proven in the alkaline cell with results shown in Fig. 3. It is clearly illustrated that a tremendous amount of CO2 was released at the anode side with a strong increase in direct correlation with increasing cell current density. At high current densities, the amount of CO2 produced at the anode was quite precisely twice the amount of produced oxygen, indicating that the majority of anionic species in the membrane was carbonate resulting precisely twice the amount of produced oxygen, indicating that the majority of anionic species in the membrane was carbonate resulting in one-half CO2 molecule released for each exchanged electron, c.f. Reaction 10, i.e. for one molecule of produced O2, two molecules of CO2 are released. At lower current densities, the fraction of CO2 was even higher, which can be explained with the fact that at low over-potentials, a certain fraction of anodic processes other than oxygen evolution, such as catalyst oxidation, contribute to the total current and, thus, result in CO2 release at the anode side without producing oxygen.

Furthermore, this CO2 pumping effect was found to occur regardless of the actual anode potential. At potentials below the equilibrium potentials for Reactions 9 and 10, this CO2 formation at the anode side can be understood in terms of a two-step process: First, the anode reaction electrochemically produces H+ species from hydrogen oxidation, which, in a subsequent chemical step, reacts with (bi)carbonate to form water and CO2, c.f. Reactions 11 and 12. This process is demonstrated by experiments with the alkaline cell using a Pt/C anode catalyst fed with H2 gas. In this case, the anode potential was close to 0 V vs. RHE, well below the equilibrium potentials of Reactions 9 and 10. Nevertheless, MS analysis of the anode exhaust gas revealed significant CO2 release at the anode side in direct correlation with the electric current density, c.f. Supplementary Information S1.2. These results show unambiguously that alkaline membrane co-electrolyzers inherently provide highly inefficient utilization of CO2 at the anode side in addition to significant contamination of the anode product gas with CO2.

Bipolar membrane and “novel configuration” co-electrolysis cells—In the previous sections, it was shown that, on the one hand, using proton exchange membranes, CO2 reduction was highly suppressed in comparison to H2 evolution, and, on the other hand, using anion exchange membranes resulted in improved CO2 reduction selectivity but also in a highly detrimental CO2 pumping from the cathode side to the anode side. One possible solution to mitigate this problem of CO2 pumping while maintaining alkaline conditions at the cathode is the use of a bipolar membrane instead of an entirely alkaline membrane. In such configuration, the alkaline anion exchange side of the membrane is facing toward the cathode and the acidic cation exchange side facing toward the anode. In principle, the acidic side of the membrane prevents the transport of (bi)carbonate species all the way to the anode. Instead, at the internal interface of the bipolar membrane between the alkaline and the acidic layers, (bi)carbonate anions react with protons from the acidic side to form water and CO2:

\[
\text{HCO}_3^- + H^+ \rightarrow H_2O + CO_2 \quad [11]
\]

\[
\text{CO}_3^{2-} + 2H^+ \rightarrow H_2O + CO_2 \quad [12]
\]

The gas analysis at the anode side of a bipolar membrane cell in full co-electrolysis operation, i.e. using IrO2-TiO2 as anode catalyst for oxygen evolution reaction, is shown in Fig. 4. It is obvious that the release of CO2 at the anode was significantly reduced, but not completely eliminated.

Moreover, the bipolar membrane cell provided similar current densities as the alkaline cell, and the CO selectivity remained at the same order of magnitude as shown in Figs. 5a and 5b. Based on these results, the use of bipolar membranes appears an attractive option for CO2 co-electrolysis. However, as argued above, CO2 and H2O are formed at the internal alkaline/acidic interface of the...
bipolar membrane. This can lead to two different problems: Firstly, the formation of CO₂ and H₂O at the internal interface of the bipolar membrane can result in the delamination of the alkaline and acidic layers. Secondly, although the CO₂ is not formed directly at the anode side, it must diffuse away from the internal interface either to the cathode or the anode side. In case of similar CO₂ diffusion properties and similar thicknesses of the alkaline and acidic layers of the bipolar membrane, it could be estimated that roughly 50% of the CO₂ formed at the alkaline/acidic interface would diffuse to the cathode side and 50% to the anode side. Thus, even with such a bipolar membrane configuration, a significant amount of CO₂ could be lost by transport from the cathode side to the anode side, as confirmed by the results in Fig. 4. In order to overcome these two issues, a novel electrochemical co-electrolysis cell configuration is proposed based on an optimal rational design approach.

This novel cell configuration is described in the Experimental section and shown in Fig. 1, and SEM images of the cathode cross-section are shown in Fig. SI3 and described in SI Section 3. The special design of the cathode catalyst layer in combination with an acidic Nafion membrane is expected to combine several advantages: Firstly, a high catalytically active surface area for the CO₂RR is provided by the “alkaline” anion exchange ionomer within the cathode catalyst layer providing an optimal alkaline environment for the reduction of CO₂, which is supplied directly from gas phase through the cathode GDL to the cathode catalyst layer. The cathode reaction selectivity for CO is shown in Fig. 5b and compared with the CO selectivities obtained using alkaline and bipolar membrane. Using this “novel configuration”, the cathode CO selectivity was not significantly changed, meaning that alkaline conditions at the cathode catalyst layer were maintained and that the additional thin film of “alkaline” anion exchange ionomer protected the cathode catalyst from direct contact with the “acidic” cation exchange membrane. This prevention of direct contact is highly important, because cathode catalyst in direct contact with the acidic membrane would strongly deteriorate the faradaic efficiency toward CO₂RR as shown in Fig. 2.

Secondly, the cation exchange membrane guarantees that the (bi)carbonate anions from the alkaline cathode ionomer are stopped from being transferred to the anode side, thus avoiding parasitic CO₂ pumping from cathode to anode side. Instead, (bi)carbonate anions are transported within the cathode alkaline ionomer only to the interface between the additional alkaline ionomer thin film and the acidic membrane where they react with protons to form H₂O and CO₂ according to Reactions 11 and 12 above. Since, as a consequence of the spray-coating preparation, the morphology of the alkaline ionomer thin film is adjusted to the rough surface of the cathode catalyst layer, its interface with the flat two-dimensional acidic membrane is established by discontinuous local contact areas. The spot-like character of this interface is highly beneficial, because CO₂ and H₂O, formed there according to Reactions 11 and 12, can laterally escape “in plane” at the perimeter of these interface spots back to the cathode electrode pore volume. In this way, both delamination of the alkaline/acidic interface and significant CO₂ diffusion to the anode side are prevented. Consequently, an almost entire suppression of parasitic CO₂ pumping to the anode side with the novel cell configuration was proven by MS analysis of the anode exhaust gas as shown in Fig. 4. Only at highest current density, very small quantities of CO₂ were detected.

Finally, the use of a cation exchange membrane provides lower electrical resistance than anion exchange membranes or bipolar membranes enabling increased energetic efficiency of the proposed co-electrolysis cell design. Thus, the high frequency resistance (HFR) of the novel configuration cell was ∼ 0.7 Ω cm² compared to ∼ 2.5 Ω cm² and ∼ 5 Ω cm² for the alkaline and bipolar cell configurations, respectively. Consequently, Fig. 5a shows that the cathode current densities were highest in the case of the novel configuration cell in comparison to the alkaline and bipolar ones.

Whereas polarization curves in Fig. 5a were measured in pseudo half-cell operation, polarization curves of full co-electrolysis cell operation with the bipolar membrane and with the novel configuration are presented in Fig. 6. The voltage efficiency of the co-electrolyzer is largely improved with the novel configuration.

Thus, the novel cell configuration combines optimal design principles regarding CO₂RR faradaic efficiency, CO₂ utilization efficiency, and energetic/voltage efficiency of the CO₂ co-electrolysis process.

**CO₂RR efficiency under different cell configurations.**—It should be pointed out that all results in Fig. 5 were obtained with the same type of cathode electrode, i.e. Au black and alkaline ionomer spray coated onto a GDL, and that the variations in CO selectivities and FE_CO₂ are not significant between the different cell configurations (see Fig 5b and Table SI 1). This confirms that the intrinsic CO₂RR selectivity is largely determined by the cathode catalyst and cathode ionomer. On the other hand, the different cell configurations revealed differences in voltage efficiency and parasitic CO₂ transport to the anode side. In order to further elucidate the connection between product selectivity/efficiency and cathode potential, the Au black catalyst activity for CO₂RR was tested in a three-electrode liquid cell under...
well-defined conditions, see details in SI section 2. The obtained CO current efficiencies are shown in Fig. 7a. Under these conditions, the Au black catalyst revealed FE(CO) up to 90% at low current densities of 0.2 mA/cm² and cathode potential of ∼−0.55 V vs RHE, but these values were quickly decreasing to 1.7% FE(CO) at 5 mA/cm² and ∼−1.4 V vs RHE. However, these results are difficult to be directly compared with the FE obtained in technical co-electrolyzer cells discussed above. If we assume that the reaction takes place at the same bulk pH in both liquid and gas-polymer electrolyte systems, then at a same electrode potential, using the same catalyst (i.e. Au black) the CO Faradaic efficiency must be in the same order of magnitude. By using the reactant in gas phase we expect to increase the current densities and not necessarily the reaction Faradaic efficiency. In Fig. 7b, the FE(CO) obtained at different cathode potentials in different media are represented. Obviously, in liquid electrolyte, at low cathode overpotentials between −0.4 and −0.8 V vs. RHE CO₂RR yielding CO appears favorable (higher FE(CO)). This result is in line with other studies of Au catalyst for CO₂RR in aqueous electrolyte using an equivalent set-up and similar reaction conditions. It is interesting to note from the data presented in Fig. 7b that at cathode potentials between ∼−1.1 and −1.5 V vs. RHE, the FE(CO) obtained in aqueous cells and in technical co-electrolysis cells were comparable. Using CO₂ from gas phase in the “novel configuration” co-electrolyzer cell, the FE(CO) were similar with the ones obtained in the liquid electrolyte cell at the same electrode potentials, but the current density values were ∼20 times larger in the novel configuration cell: At ∼−1.1 V vs. RHE, the current values were −0.2 mA/cm² in the liquid cell and −50 mA/cm² in the latter, and at ∼−1.5 V vs. RHE, −5 mA/cm² and −100 mA/cm² were obtained, respectively. However, in a perspective of increasing the CO production rate when using this co-electrolysis process, a catalyst with a large potential window of high FE(CO) values appears more suitable.

**Fundamental current transport properties of the alkaline-acidic ionomer junction.**—As discussed in detail above, the intrinsic cell configuration for efficient CO₂RR must be bipolar with an alkaline environment at the cathode side and an acidic part that blocks the CO₂ transport to the anode side. From this perspective, also the “novel configuration” could be classified as “bipolar” although no bipolar membrane was used. At this point, the question arises whether a multipolar system with more than two different electrolyte layers could even be superior to the bipolar system. For instance, it could be tempting to provide an alkaline environment also at the anode side from the motivation to enable the use of less costly anode catalysts for the oxygen evolution reaction, which would result in an alkaline-acidic-alkaline tri-layer cell structure. From the same motivation, in a recently published study the authors investigated where a bipolar membrane was used in opposite direction to the present work, i.e. with the alkaline side facing toward the anode. As shown in the following, such bi- or multi-polar (co)-electrolysis systems with an alkaline environment at the anode side must suffer from an intrinsically inferior voltage efficiency, which can be understood from the fundamental current transport properties of the alkaline-acidic electrolyte junction.

In any bipolar alkaline-acidic system, the interface between the two opposite types of polymer electrolytes is the critical part from the perspective of the current transport properties. The fundamental behavior of an alkaline-acidic ionomer junction can be regarded as an ionic analogue of an electronic semiconductor p-n junction: The cation conductive “acidic” ionomer provides positive mobile charge carriers, such as protons, and, vice versa, the anion conductive “alkaline” ionomer provides negative mobile charge carriers, such as hydroxide ions or (bi)carbonate. Depending on the current direction,
these mobile ions either recombine at the alkaline-acidic interface to produce H₂O (plus CO₂ in case of (bi)carbonate), or they must be generated at this interface by (auto)protolysis of H₂O. These fundamental ion transport properties of the bipolar membrane and the "novel" configuration systems were confirmed by "H₂ pump" experiments. For this purpose, Pt/C electrodes were applied both as cathode and as anode with similar Pt loadings on each electrode (see detailed experimental description in SI Section 4). The results are presented in Fig. 8. When the systems are operated in forward bias, i.e. alkaline side at the cathode, the current densities are significantly higher than in reverse bias orientation with the acidic side at the cathode. This behavior is also observed for the bipolar membrane system even though the commercial bipolar membrane contains a catalyst layer at its internal interface designed to improve the water autoprotolysis. Still, this effect is most dramatic for the novel configuration system, where no such catalytic layer was used at the alkaline–acidic interface. These experimental results confirm the "ionic diode" behavior of the alkaline–acidic junction in both systems. Moreover, they prove that in the case of the novel configuration system, the additional thin film of alkaline ionomer successfully prevented direct contact between cathode catalyst and the Nafion membrane, because such direct contact would bypass the alkaline-acidic junction and strongly decrease the asymmetry between the polarization curves for both orientations.

The novel cell configuration operating in the reverse bias mode appears like a suitable solution for further industrialization of a co-electrolyzer. Despite the fact that the OER will take place in acidic conditions where expensive catalysts are needed, a series of advantages (e.g. preserved cathode selectivity to CO at high pH, suppressed parasitic CO₂ pumping at the anode, improved overall cell voltage efficiency) demonstrate this configuration for an applicability in an industrial process. However, to reach the industrialization step, aspects related to long term operation must be addressed and discussed.

Stability properties.—The stability of the novel configuration cell and of the bipolar membrane cell was also investigated. Fig. 9 shows the stability behavior of the two systems operated at −50 mA/cm² for a total of 22 hours. Firstly, the cells were continuously operated for 21 hours, cf. “operation 1” region in Fig. 9. For both systems, it was observed that the CO selectivity was strongly decreasing during the first 5 hours of operation. After that, no significant CO signal was detected with H₂ being the only reaction product detected. For the novel configuration cell, the cathode potential decreased after 5h operation while for the bipolar membrane cell, the cathode potential increased after 5h of operation.

After drying of the cathodes 24 hours in order to remove accumulated water, the cells were operated under the same experimental conditions for an additional hour. These results are presented Fig. 9 region “operation 2”. For both systems, the cathode potentials returned to around the initial values and CO was detected again with CO selectivity values very close to the initial ones. These values were stable for approx. 30 min before the CO signals started to decrease again.

This behavior of both systems can be related to the fact that an excess of water molecules are formed at the alkaline–acidic interface according to Reactions 11 and 12. Most of this water, especially for the novel configuration cell, the cathode potential decreased after 5h operation while for the bipolar membrane cell, the cathode potential increased after 5h of operation.

After drying of the cathodes 24 hours in order to remove accumulated water, the cells were operated under the same experimental conditions for an additional hour. These results are presented Fig. 9 region “operation 2”. For both systems, the cathode potentials returned to around the initial values and CO was detected again with CO selectivity values very close to the initial ones. These values were stable for approx. 30 min before the CO signals started to decrease again.

This behavior of both systems can be related to the fact that an excess of water molecules are formed at the alkaline–acidic interface according to Reactions 11 and 12. Most of this water, especially for the novel configuration cell, diffuses to the cathode where it accumulates during operation, thus resulting in cathode flooding. Consequently, the cathode catalyst layer is progressively blocked with water and the CO₂RR reactant, CO₂ gas, cannot access the catalyst surface anymore. At this point, only H₂ can still be produced at the cathode. After drying, the CO₂ gas can reach the cathode catalyst again and the cell performance is recovered. This observed recovery proves that the MEA components (e.g. cathode catalyst, alkaline ionomer layer, membrane) are not significantly degraded during the 22 h of operation. Further studies will be performed in the near future to improve during stable continuous operation by a carefully controlled water management.

Figure 8. “H₂ pump” experiments to evaluate alkaline-acidic junction characteristics of the bipolar membrane (a) and novel configuration (b) systems operated in different orientations. Anode and cathode electrodes were symmetric and based on Pt/C catalyst, and both were fed with fully humidified H₂. The measurements were performed at 40 ºC and ambient pressure.
Key elements for efficient electrochemical CO₂ reduction from gas phase in a non-liquid electrolyte cell were identified and combined in a rational design of an optimal co-electrolysis cell configuration. Whereas the competition between CO₂-RR and HER requires alkaline environment at the cathode side in order to achieve high CO₂-RR selectivity, an all-alkaline cell was shown to lead to tremendous parasitic CO₂ pumping from the cathode to the anode side. Therefore, in order to preserve high CO₂ utilization efficiency, a bipolar design approach must be used with an alkaline side at the cathode and an acidic part that blocks the parasitic CO₂ transport to the anode side. Consequently, a cell configuration with a bipolar membrane demonstrated a significant decrease of CO₂ release at the anode side while maintaining good selectivity for the reduction of CO₂. However, a principal limitation of the bipolar membrane configuration was identified and attributed to the formation of water and CO₂ at the internal alkaline-acidic interface of the bipolar membrane, which could result in membrane delamination.

Combining all key requirements in an optimal way, a novel cell configuration was developed containing alkaline ionomer within the cathode catalyst layer, a standard Nafion membrane, and an additional thin film of alkaline ionomer sprayed on top of the cathode catalyst layer in order to protect the latter from the acidity of the Nafion membrane. With this novel cell configuration, the CO₂-RR faradaic efficiency of the alkaline environment was preserved, the parasitic CO₂ pumping to the anode side was completely suppressed, faradaic efficiency of the alkaline environment was preserved, the parasitic CO₂ pumping from the cathode to the anode side. Therefore, in order to preserve high CO₂ utilization efficiency, a bipolar design approach must be used with an alkaline side at the cathode and an acidic part that blocks the parasitic CO₂ transport to the anode side. Consequently, a cell configuration with a bipolar membrane demonstrated a significant decrease of CO₂ release at the anode side while maintaining good selectivity for the reduction of CO₂. However, a principal limitation of the bipolar membrane configuration was identified and attributed to the formation of water and CO₂ at the internal alkaline-acidic interface of the bipolar membrane, which could result in membrane delamination.

Combining all key requirements in an optimal way, a novel cell configuration was designed allowing for high selectivity at the cathode side in order to achieve high CO₂-RR selectivity, an all-alkaline cell was shown to lead to tremendous parasitic CO₂ pumping from the cathode to the anode side. Therefore, in order to preserve high CO₂ utilization efficiency, a bipolar design approach must be used with an alkaline side at the cathode and an acidic part that blocks the parasitic CO₂ transport to the anode side. Consequently, a cell configuration with a bipolar membrane demonstrated a significant decrease of CO₂ release at the anode side while maintaining good selectivity for the reduction of CO₂. However, a principal limitation of the bipolar membrane configuration was identified and attributed to the formation of water and CO₂ at the internal alkaline-acidic interface of the bipolar membrane, which could result in membrane delamination.

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17. S. Ma, M. Sadakyo, R. Luo, M. Heima, M. Yamanchi, and P. J. A. Kenis, “One-step
electrosynthesis of ethylene and ethanol from CO2 in an alkaline electrolyzer.” J
Power Sources, 301, 219 (2016).
18. J. Albo and A. Irabien, “Cu2O-loaded gas diffusion electrodes for the continuous
electrochemical reduction of CO2 to methanol.” J Catal, 343, 232 (2016).
19. J. Albo, A. Sáez, J. Solla-Gullón, V. Montiel, and A. Irabien, “Production of methanol
from CO2 electroreduction at Cu2O and Cu2O/ZnO-based electrodes in aqueous
solution.” Appl Catal B: Environ, 176-177, 709 (2015).
20. J. Albo, D. Vallego, G. Beobide, O. Castillo, P. Castro, and A. Irabien, “Copper-Based
Metal–Organic Porous Materials for CO2 Electrocatalytic Reduction to Alcohols.”
ChemSusChem, 10, 1100 (2017).
21. S. Pérez-Rodríguez, F. Barreras, E. Pastor, and M. J. Lázaro, “Electrochemical reac-
tors for CO2 reduction: From acid media to gas phase.” Int J Hydrogen Energy, 41,
19756 (2016).
22. Z. Liu, R. I. Masel, Q. Chen, R. Kutz, H. Yang, K. Lewinski et al. “Electrochemical
generation of syngas from water and carbon dioxide at industrially important rates.”
J CO2 Util, 15, 50 (2016).
23. C. Delacourt, P. L. Ridgway, J. B. Kerr, and J. Newman, “Design of an Electro-
chemical Cell Making Syngas CO+H2 from CO2 and H2O Reduction at Room
Temperature.” J Electrochem Soc, 155, E42 (2008).
24. R. B. Kutz, Q. Chen, H. Yang, S. D. Sajjad, Z. Liu, and I. R. Masel, “Sustain-
ion Imidazolium-Functionalized Polymers for Carbon Dioxide Electrolysis.” Energy
Technol, 5, 929 (2017).
25. I Merino-García, J. Albo, and A. Irabien, “Tailoring gas-phase CO2 electore-
duction selectivity to hydrocarbons at Cu nanoparticles.” Nanotechnology, 29
(2018).
26. I. Merino-García, J. Albo, and A. Irabien, “Productivity and Selectivity of Gas-Phase
CO2 Electroreduction to Methane at Copper Nanoparticle-Based Electrodes.” Energy
Technol, 5, 922 (2017).
27. D. A. Salvatore, D. M. Weekes, J. He, K. E. Dettelbach, Y. C. Li, T. E. Mallouk et al.
“Electrolysis of Gaseous CO2 to CO in a Flow Cell with a Bipolar Membrane.” ACS
Energy Lett, 149 (2017).
28. Y. Fang and J. C. Fleyfel, “Electrochemical Reduction of CO2 at Functionalized Au
Electrodes.” J Am Chem Soc, 139, 3399 (2017).
29. X. Jiang, F. Cai, D. Guo, J. Dong, S. Miao, G. Wang et al. “Electrocatalytic reduction
of carbon dioxide over reduced nanoporous zinc oxide.” Electrochem Commun, 68,
67 (2016).
30. A. Pátru, A. Rabis, S. E. Temmel, R. Kotz, and T. J. Schmidt, “Pt/IrO2–TiO2 cathode
 catalyst for low temperature polymer electrolyte fuel cell – Application in MEAs,
performance and stability issues.” Catal Today, 262, 20 (2015).
31. A. Pátru, T. Binninger, B. Pribyl, and T. J. Schmidt, Pat. application number. WO
2017/P15439 F5318. 1 (2016).
32. T. Binninger, B. Pribyl, A. Patru, and P. Ruettmann, “Multivariate calibration method
for mass spectrometry of interfering gases such as mixtures of CO, N2, and CO2.” J
Mass Spectrom, (2018).
33. Y. Chen, C. W. Li, and M. W. Kanan, “Aqueous CO2 Reduction at Very Low Over-
potential Aqueous CO 2 Reduction at Very Low Overpotential on Ox- ide-Derived
Au Nanoparticles.” J Am Chem Soc, 134, 19969 (2012).
34. J. W. Vickers, D. Alfonso, and D. R. Kaufman, “Electrochemical Carbon Dioxide
Reduction at Nanostructured Gold, Copper, and Alloy Materials.” Energy Technol,
5, 775 (2017).
35. K. P. Kuhl, E. Cave, D. N. Abream, and T. F. Jaramillo, “New Insights into the Elec-
trochemical Reduction of Carbon Dioxide on Metallic Copper Surfaces.” Energy
Environ Sci, 5, 7050 (2012).
36. H. Yang, J. J. Kacurz, S. D. Sajjad, and R. I. Masel, Electrochemical conversion of
CO2 to formic acid utilizing Sustainion membranes.” J CO2 Util, 20, 208 (2017).
37. E. R. Cave, J. H. Montoya, K. P. Kuhl, D. N. Abream, T. Hatsukade, C. Shi et al.
“Electrochemical CO2 reduction on Au surfaces: mechanistic aspects regarding the
formation of major and minor products | 15856 (2017).
38. M. Unlu, J. Zhou, and P. A. Kohl, “Hybrid anion and proton exchange membrane
fuel cells.” J Phys Chem C, 113, 11416 (2009).
39. J. M. Abilfield, L. Liu, and P. A. Kohl, “PEM/AEM Junction Design for Bipolar
Membrane Fuel Cells.” J Electrochem Soc, 164, F1165 (2017).
40. A. Malti, E. O. Gabrielssson, X. Crispin, and M. Berggren, “An Electrochromic Bip-
olar Membrane Diode.” Adv Mater, 27, 3909 (2015).
41. D. A. Vermaas, M. Sassenburg, and W. A. Smith, “Photo-assisted water splitting with
bipolar membrane induced pH gradients for practical solar fuel devices.” J Mater
Chem A, 3, 19556 (2015).
42. H. Strathmann, J. J. Krol, H. J. Rapp, and G. Eigenberger, “Limiting current density
and water dissociation in bipolar membranes.” J Membr Sci, 125, 233 (1997).
43. E. O. Gabrielssson, K. Tybrandt, and M. Berggren, “Ion diode logics for pH control.”
Lab Chip, 12, 2507 (2012).
44. C. Shen, R. Wyczisk, and P. N. Pintauro, “High performance electrosyn bipolar
membrane with a 3D junction.” Energy Environ Sci, 10, 1435 (2017).