

Review

A Review of the Use of Immobilized Ionic Liquids in the Electrochemical Conversion of CO₂

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Abstract: This paper is a review on the application of imidazolium-based ionic liquids tethered to polymer backbones in the electrochemical conversion of CO₂ to carbon monoxide and formic acid. These tethered ionic liquids have been incorporated into novel anion ion exchange membranes for CO₂ electrolysis, as well as for ionomers that have been incorporated into the cathode catalyst layer, providing a co-catalyst for the reduction reaction. In using these tethered ionic liquids in the cathode catalyst composition, the cell operating current increased by a factor of two or more. The Faradaic efficiencies also increased by 20–30%. This paper provides a review of the literature, in addition to providing some new experimental results from Dioxide Materials, in the electrochemical conversion of CO₂ to CO and formic acid.

Keywords: anion exchange membranes; electrochemical; formic acid; carbon monoxide; CO₂ utilization; ionic liquids; alkaline water electrolysis

1. Introduction

This paper is a review of the application of imidazolium-based ionic liquids tethered to polymer backbones in the electrochemical conversion of CO₂ to carbon monoxide and formic acid. The work started in 2011, when Rosen et al. [1] found that the addition of 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIM⁺BF₄⁻) or 1-Ethyl-3-methylimidazolium chloride (EMIM⁺Cl⁻) reduced the overpotential for CO₂ electrolysis by almost a volt. The ionic liquids also helped increase the selectivity of CO₂ to CO to above 95% [1–5]. Further investigation into whether the imidazolium cation was a promoter or co-catalyst in the heterogeneous/homogeneous electrocatalysis of CO₂ reduction was conducted by Zhao et al. [6]. They found that imidazolium, as well as pyrrolidinium, did enhance the reduction reaction with Ag as a co-electrocatalyst, especially in the presence of water.

Many investigators have been building on these findings, with the results being difficult to translate into practical devices. The presence of the ionic liquid in the solution inhibited CO₂ mass transfer into the cathode catalyst layer. Furthermore, the electrochemical cells lost most of their activity in less than about 500 h, due to the degradation of these ionic liquids. To help resolve these stability issues, researchers began investigating and synthesizing various substituted ionic liquids and determining their stability, especially in alkaline solutions. They have also been experimentally incorporating these ionic liquids, using various polymerization methods, in the search for producing alkaline stable anion exchange membranes. Some of this work is summarized below.

Hugar et al. synthesized a series of imidazolium organic cations, evaluating the impact of substitution on the imidazolium ring and its chemical stability in 1, 2, and 5 M KOH at 80 °C in 30-day tests. They found that C4- and C5- substitutions in the imidazole ring with methyl groups were

important to achieving alkaline stability. The methyl group(s) improved the ionic liquid ring stability and were better than similar substitutions using phenol groups [7].

Ye et al. investigated several synthesized polymerized imidazoliums, such as poly(1-[(2-methacryloyloxy)ethyl]-3-butylimidazolium hydroxide), under high-temperature alkaline conditions, finding significant degradation in their prepared imidazoliums in 1 M and 6 M KOH in 24- to 168-h tests [8].

Si et al. researched the alkaline stability of imidazolium cations having butyl groups at various substitution positions (N1-, C2-, and N3-), finding that the C2- substituted cations had a better alkaline stability in 1 M KOH in 240-h tests [9]. In addition, they also prepared cast anion exchange membranes by photo-crosslinking a mix of acrylonitrile/styrene, divinylbenzene, and photo-initiator using selected imidazolium cations. The C2- substituted [C2-BBMIM]⁺ imidazolium cation incorporated into the anion ion exchange membranes that they prepared showed stable conductivities after 240 h in 1 M KOH at 80 °C [9].

Qiu et al. investigated the cross-linking synthesis of styrene and acrylonitrile with various alkaline imidazolium-type ionic liquids in the search for making alkaline stable anion ion exchange membranes. A variety of photo-crosslinked membranes were made, using 1-methyl-3-(4-vinylbenzyl) imidazolium chloride as the ionic liquid. The membrane conductivity stability versus time in 1 and 10 M KOH solutions were evaluated, showing stable conductivity for up to 1000 h in 1 M KOH at 60 °C [10]. The same group also did a further study, converting 1-butyl-2-methylimidazole and 1-allyl-2-methylimidazolebromide to bis-imidazoliums using bromine-based compounds and photo-crosslinking them. They produced several anion membranes with stable conductivity in 1 M KOH at 60 °C for 30 days [11].

Guo et al. prepared a novel set of anion exchange membranes based on the copolymers of 1-allyl-3-methylimidazolium chloride (AmimCl) ionic liquid with either methyl methacrylate (MMA) or butyl methacrylate (BMA), which were prepared via free radical polymerization. The anion membranes were found to be stable in 6 M NaOH for 120 h at 60 °C [12].

Marinkas et al. worked on synthesizing a series of anion conducting polymers (PPO-BIM) based on a poly-(2,6-dimethyl-1,4-phenylene oxide) (PPO) backbone and methylated 2-mesitylbenzimidazol (BIM) functional groups. The membranes were operated in a water electrolysis cell, where the membranes were found to be stable in 0.5 M KOH at 50 °C, but not in 1 M KOH at 80 °C [13].

Tham et al. looked at the effect of substituents at the C2- and N3- positions of the imidazolium functional group of the poly(arylene ether) ketone-based anion electrolyte membranes that they prepared. The synthesized anion membranes were operated in alkaline water electrolysis zero gap cells in order to evaluate membrane and cell performance. They were able to operate the water electrolysis cell at 1.9 V at 500 mA/cm². The simultaneous use of C2- methyl and N3- butyl substituents in the PAEK-APMBI membrane resulted in good chemical stability in 10 wt% NaOH at 60 °C, which retained 97% of its ion exchange capacity after 28 days [14].

Recognizing these difficulties in ionic liquid alkaline stability as well as to the need for alkaline stable anion membranes, Masel et al. [15–20] developed a new membrane system where the cation imidazoliums are tethered to a polymer backbone, as shown in Figure 1. These novel ionomers and membranes that were developed are now marketed under the Sustainion[®] tradename. Other investigators, as previously discussed, have been working on different approaches in the preparation of anion membranes, using different polymer mixture components, polymer backbones, and various ionic liquids [9–14]. Unfortunately, there is no comparison data available for those and other membranes in a direct comparison with the Sustainion[®] membranes in CO₂ reduction to CO.

The experimental results with the Sustainion[®]-based system were a set of ionomers and membranes that were stable for at least 12,000 h at 60 °C in 1 M KOH, as shown in Figure 2. Presently, these membranes are being evaluated by multiple investigators [21–29]. This paper briefly reviews the results in the CO₂ conversion to CO as well as in the conversion to formic acid. Also included is a comparison set of data for the same electrochemical processes with membranes other than Sustainion[®],

with a particular focus on studies where the cells had been run for at least 100 h, as summarized by Nwabara et al. [30].

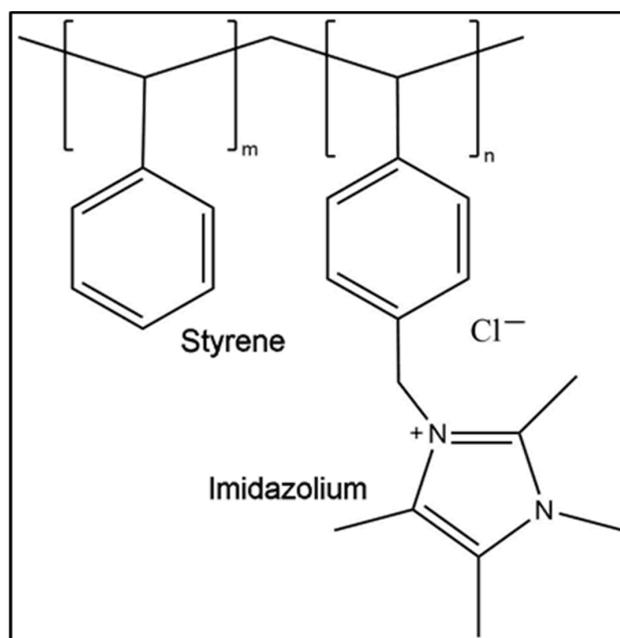


Figure 1. The structure of Sustainion[®] membranes where an imidazolium-based cation is attached to a styrene backbone to create an immobilized ionic liquid material.

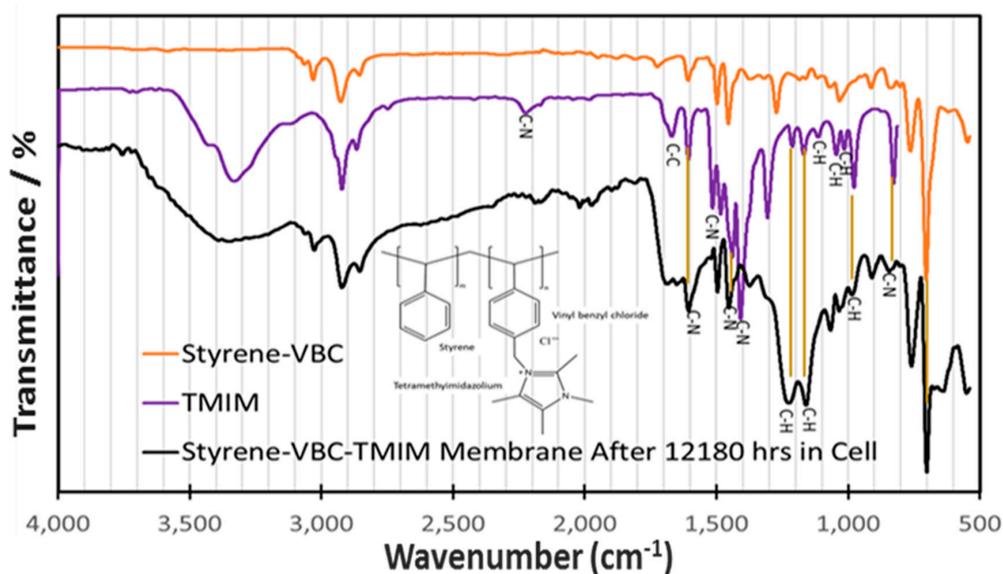


Figure 2. Infrared spectrum of (top) the styrene-vinyl benzyl chloride (VBC) copolymer that is used for membrane synthesis; (middle) tetramethyl imidazole (TMIM), the other component used in the membrane synthesis; (bottom) the active area of the ePTFE supported Sustainion[®] X37-T membrane. The spectrum was taken after removing the membrane from the alkaline exchange membrane (AEM) water electrolyzer after operating at 60 °C in 1 M KOH for 12,180 h, and carefully cleaning the membrane for the FTIR tests.

2. Immobilizing Ionic Liquids to Create Functionalized Anion Conducting Membranes

Figure 1 shows the structure of the Sustainion[®] polymers and ionomers that Dioxide Materials has made. It consists of an imidazolium cation tethered to a styrene backbone. In one of the original

membrane formulations, called polystyrene vinylbenzyl methyl imidazolium chloride (PSMIM), methyl imidazolium was used as the functional group. Later, 1,2,4,5-Tetramethylimidazole was employed as the functional group. This formulation, named PSTMIM, was further improved, producing the commercial anion membrane form designated as Sustainion[®] X-37.

The Sustainion[®] anion exchange membranes were found to be surprisingly stable under alkaline conditions. A Thermo Nicolet FTIR Spectrometer with a resolution of 4 cm^{-1} and scan range of $500\text{--}4000\text{ cm}^{-1}$ using an ATR mode was used to check the Sustainion[®] membranes for any degradation. Figure 2 shows the FTIR spectrum of the membrane after 12,180 h of operation in an alkaline exchange membrane (AEM) water electrolyzer running in 1 M KOH at $60\text{ }^{\circ}\text{C}$. It also shows the spectra of the two components that are used to synthesize the membrane: (i) a copolymer of styrene and vinyl benzyl chloride, and (ii) tetramethylimidazole (TMIM). The membrane structure is shown as an inset. Notice that the TMIM C-N ring modes at 1605 , 1435 , and 825 cm^{-1} and the TMIM CH_3 stretches at 1211 , 1165 , and 975 cm^{-1} are still present in the membrane. The feature at 1403 cm^{-1} in the TMIM spectrum is missing from the spectrum of the membrane. This mode is associated with out of plane bending around the α -nitrogen in TMIM and had disappeared, since the α -nitrogen is now bound to the benzyl ligand. Other measurements showed that the membrane conductivity was unchanged during this run. Clearly, the membrane is stable under alkaline conditions.

3. Electrochemical Conversion of CO_2 to CO

Sustainion[®] membranes have been used by various investigators in the electrochemical conversion of CO_2 to CO. Figure 3 shows a schematic of an electrolyzer for CO_2 electrolysis to CO. The cell uses a titanium flow field on the anode and a 316 L stainless steel serpentine flow field on the cathode. The anode is made by depositing a mixture of IrO_2 nanoparticles and a Nafion solution binder onto a Toray carbon paper, as described elsewhere [4,17,31]. The cathode was made by depositing a mixture of Ag nanoparticles and Sustainion[®] XA-9 ionomer binder onto a Sigracet 39 BC GDL carbon paper, as described elsewhere, to make the gas diffusion electrode (GDE) [4,17,31]. The membrane evaluated is typically Sustainion[®] X-37.

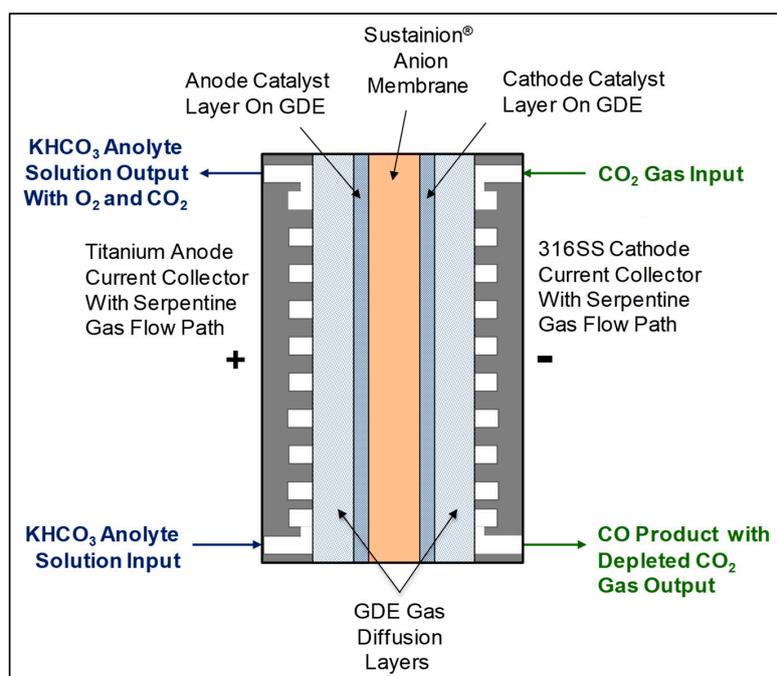


Figure 3. The configuration of a Dioxide Materials single-cell electrolyzer for CO_2 conversion to CO with an active area of 250 cm^2 .

Figure 4 shows some of the typical data. In this case, 1 L/min of humidified CO₂ was fed into a single cell electrolyzer with an active area of 250 cm². The cell voltage was first fixed at 3.3 V, and the current reached 50 A (200 mA/cm²) in less than 1 h. Then, the current was fixed at 50 A, and the cell voltage and CO selectivity monitored with time. Figure 4 shows the cell voltage and CO selectivity of the 250 cm² CO₂ electrolyzer operating at 200 mA/cm² and 35 °C. The results show that the cell voltage stabilized at 3.05 V for over 120 h, maintaining CO selectivity at 97–98%.

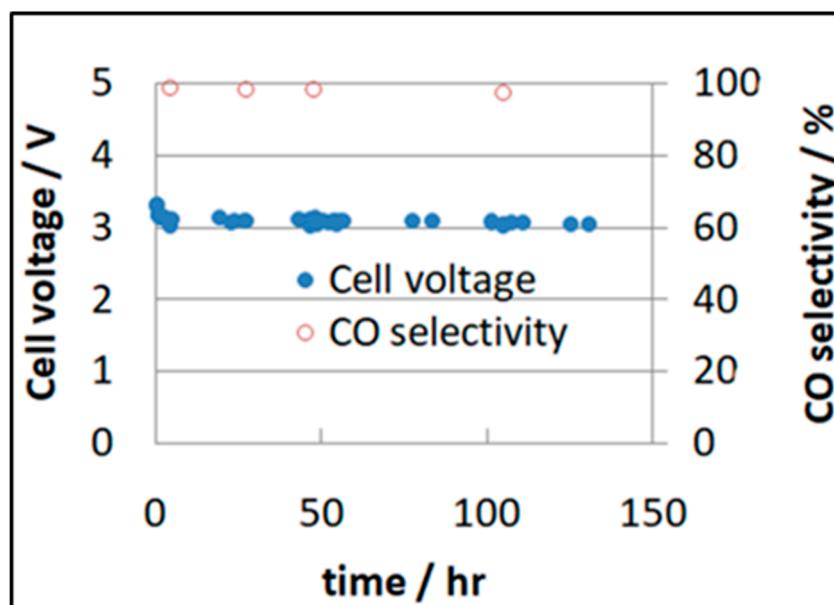


Figure 4. Cell voltage and CO selectivity of the 250 cm² CO₂ electrolyzer as a function of time, 200 mA/cm² and 35 °C. Humidified CO₂ was metered to the cathode at 1 L/min. The anolyte was a 20 mM KHCO₃ circulated through anode at a flowrate of 0.6 L/min.

Table 1 summarizes the data on the electrochemical conversion of CO₂ to CO and O₂ using Sustainion[®] membranes. Also included is a selection of examples from the literature where different membranes were used. Notice that the current is higher when the Sustainion[®] anion membranes are used, only needing a lower voltage to maintain the same equivalent current density.

Table 1. A selection of data comparing the electrolysis of CO₂ to CO using Sustainion[®] anion membranes and other alternatives.

References	Cell Configuration			Cell Area cm ²	Cell Voltage V	Current Density mA/cm ²	CO Selectivity %	Run Length h
	Anode/Catalyst	Cathode/Catalysts	Membrane					
Kutz et al. [20]	Nano IrO ₂ on GDE	Nano Ag on GDE/PSMIM ionomer	Sustainion [®] PSMIM	5	2.8–3.0	50	85–95%	4500
	Nano IrO ₂ on GDE	Nano Ag on GDE/XA-9 ionomer	Sustainion [®] PSTMIM	5	2.8–3.0	200	85–95%	1000
Liu et al. [28]	Nano IrO ₂ on GDE	Nano Ag on GDE/XA-9 ionomer	Sustainion [®] X37-50	5	2.8–3.0	200	90–95%	3800
	Nano IrO ₂ on GDE	Nano Ag on GDE/XA-9 ionomer	Sustainion [®] X37-50	5	2.8–3.0	600	93–96%	4
Kaczur et al. [32]	Nano IrO ₂ on GDE	Nano Ag on GDE/XA-9 ionomer	Sustainion [®] X37-50	250	2.8–3.0	120	98%	760
Endrődi et al. [21]	IrO ₂ catalyst on Ti Frit	Nano Ag on GDE/XA-9 ionomer	Sustainion [®] X37T	61 cm ² each cell, 3 cell stack	2.75–3.0	200–300	70–85%	8–100
Jeong et al. [22]	Nano IrO ₂ on GDE	Ni-SA-NCs on GDE	Sustainion [®] X37-50	5	2.60 3.00	140 380	99% 99%	9 9
Lee et al. [23]	Catalyst on Ti Felt	Nano Pd, Ag, Zn on GDE/XA-9 ionomer	Sustainion [®] X37-50	5	3.0	200	96.7%	10
Wang et al. [25]	Pt/Ti alloy	Cobalt phthalocyanine catalysts CoPc1 and CoPc2	Sustainion [®] X37-50	10	-	22–165	92–94%	2
Ren et al. [24]	Nickel Foam	Cobalt phthalocyanine	Sustainion [®] X37-50	4	2.5	150	95%	3–5
Masel et al. [31]	Nano RuO ₂ or IrO ₂ on GDE	Nano Ag on GDE /PSMIM ionomer	Sustainion [®] PSMIM	5	3.0	600	95%	8
Haas et al. [33]	IrO ₂ on titanium	Ag-Based GDE w/o Carbon	ZrO ₂ -based Diaphragm	10	4.90	150	82–88%	-
	IrO ₂ on titanium	Ag-Based GDE w/o Carbon	ZrO ₂ -based Diaphragm	10	7.0–7.5	300	60%	1250
	IrO ₂ on titanium	Ag-Based GDE w/o Carbon	Nafion	10	3.20 (30 °C)	50	45–60%	1000
	IrO ₂ on titanium	Ag-Based GDE w/o Carbon	Nafion	10	4.80 (30 °C)	150	60%	250

4. Electrochemical Conversion of CO₂ to Formic Acid

The highly conductive properties of the Sustainion[®] anion ion exchange membrane allowed the development of a unique three-compartment cell, as shown in Figure 5, that can generate pure formic acid at high concentrations. The system requires only deionized water and CO₂ gas. The cell design uses a GDE cathode consisting of a nanoparticle tin oxide catalyst and carbon, using Sustainion[®] XA-9 ionomer as a binder. The CO₂ is reduced to the formate ion (HCOO⁻) on the cathode, which then passes through the anion membrane into the center compartment [32,34,35].

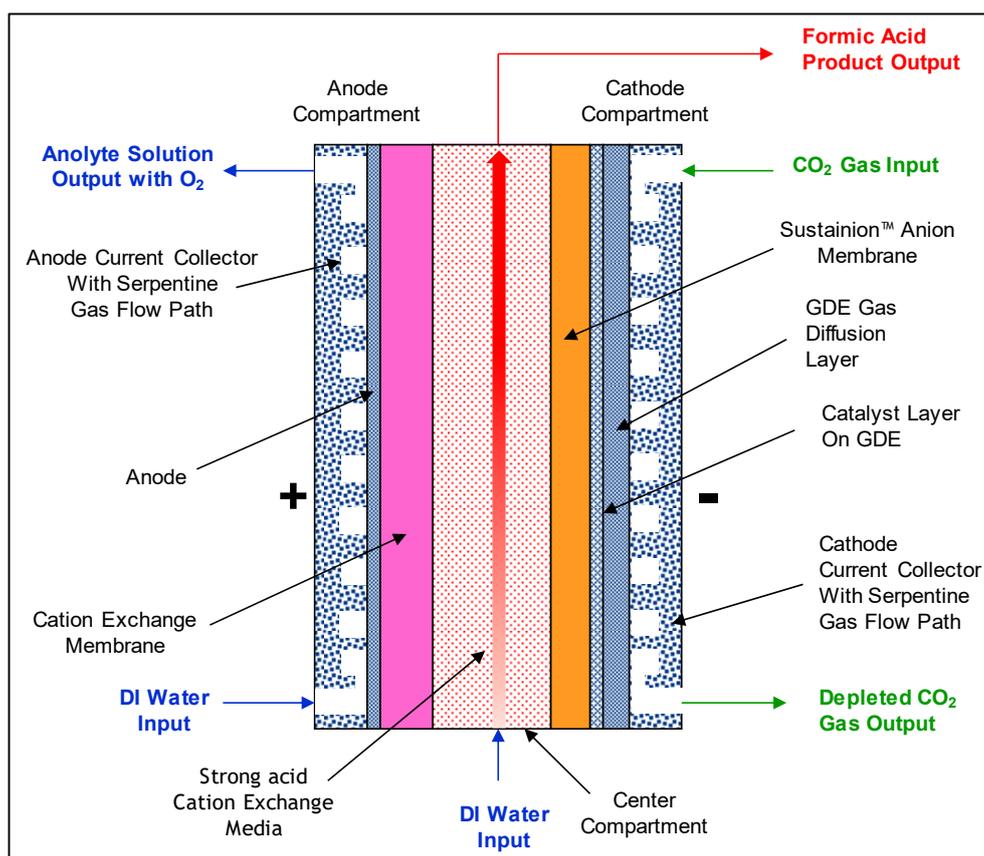


Figure 5. The design of a three-compartment electrolyzer cell that converts CO₂ and water into formic acid.

The GDE anode consists of a nanoparticle IrO₂ catalyst or an IrO₂ thermal coating on sintered titanium fiber paper, in converting water into H⁺ ions and oxygen (O₂). The H⁺ ions pass through the adjoining cation ion exchange membrane into the center flow compartment. The H⁺ and formate ions combine in the center compartment, directly forming a formic acid product, which is removed from the compartment using a deionized water input stream. Formic acid product concentrations of up to about 20 wt% have been produced.

Figure 6 shows an example of the performance of a 5 cm² cell operating for 500 h, evaluating a new potential candidate cathode electrocatalyst at a current density of 200 mA/cm², and producing a 10 wt% formic acid product. The operating cell voltage was constant at 3.5 V.

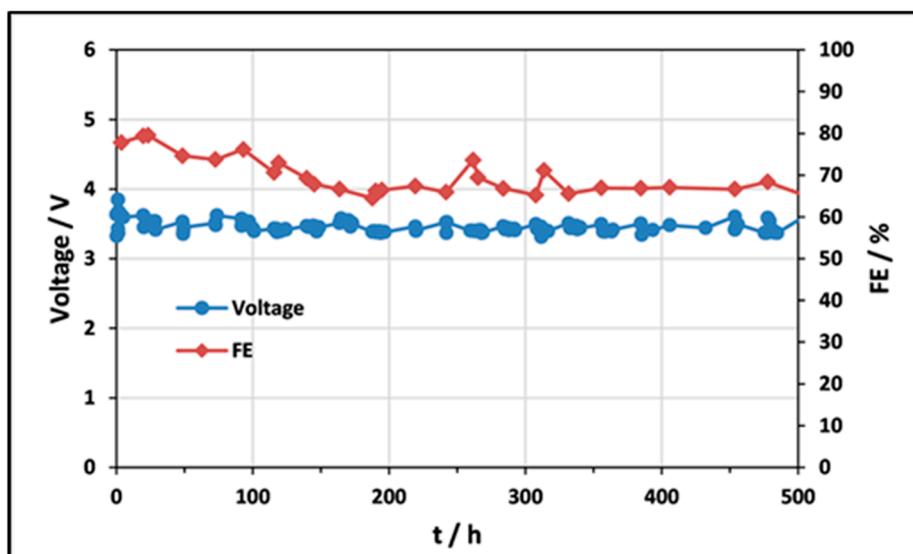


Figure 6. The performance of a 5 cm² formic acid test cell, producing 10 wt% formic acid operating at 200 mA/cm², with a candidate cathode electrocatalyst.

Table 2 summarizes a number of examples of electrochemical CO₂ to formic acid cell data found in the literature. A number of the electrochemical cell configurations in these papers generate formate salts, and are not included in the table. Notice that the current is higher when Sustainion[®] membranes are used, requiring only a lower voltage to maintain the same current.

Table 2. A selection of data comparing the electrolysis of CO₂ and H₂O to formic acid/formate using Sustainion® anion membranes and other membrane alternatives.

References	Cell Configuration				Cell Area	Cell Voltage V	Current Density mA/cm ²	Formic Acid Wt%	FE %	Run Length h
	Anode/Catalyst	Cathode/Catalysts	Membrane							
			Anode Side	Cathode Side						
Yang et al. [34]	Graphite/Nano IrO ₂ on GDE	Nano Sn on GDE with PSMIM ionomer	Nafion 212	Sustainion® X37-50	5	3.3–3.4	140	15%–18%	30%	550
Yang et al. [34,35] Kaczur et al. [32]	Titanium/Ti Fiber Paper with IrO ₂	Nano Sn on GDE with PSMIM ionomer	Nafion 324	Sustainion® X37-50	5	3.5	140	10%	80% → 94%	142
This Paper	Titanium/Ti Fiber Paper coated with IrO ₂	Nano XX catalyst on GDE with PSMIM ionomer	Nafion 324	Sustainion® X37-50	5	3.5	200	10%	80% → 65%	500
Xia et al. [36]	Graphite/IrO ₂ on Carbon	2D-Bismuth	Nafion (1110)	Sustainion® X37-50	4	3.0	30	0.5%	80%	100
Lee et al. [37]	Nano Pt on Carbon	Nano Sn on GDE with Nafion ionomer	Nafion 115	-	9	Cathode Potential Constant: −0.7 V	5–20	Formic Acid Vapor	12.5% → 7.0%	3–10
Lei et al. [38]	Not specified	Nano Sn on GDE with Nafion ionomer	Toray A901 (anion)	-	25	3 → 5	5 → 100	Formate	80% → 15%	2
	Not specified	Nano Sn on GDE with Nafion ionomer	Yichen (anion)	-	25	3 → 5	5 → 100	Formate	80% → 12%	2
	Not specified	Nano Sn on GDE with Nafion ionomer	FAD (anion)	-	25	3 → 5	5 → 100	Formate	85% → 12%	2
	Not specified	Nano Sn on GDE with Nafion ionomer	Nafion 117 Cation	-	25	3 → 5	5 → 100	Formate	85% → 16%	2
Ramdin et al. [39]	Not specified	Sn electrode	Fumatech Bipolar FBM-PK	-	80	4.0	60 @50 bar CO ₂	Formate 12500 ppm	80%	0.33
	Not specified	Sn electrode	Fumatech FKB-PK (cation)	-	80	3.5	40 @50 bar CO ₂	Formate 9000 ppm	80%	0.33
	Not specified	Sn electrode	Fumatech Bipolar FBM-PK	Fumatech Bipolar FBM-PK	80	3.5	30 @50 bar CO ₂	1.0%	90%	0.33

5. Summary

Laboratory test results showing that specific ionic liquids can reduce the overpotential in the electrochemical reduction of CO₂ led to the development of the Sustainion[®] anion ion exchange membranes by researchers at Dioxide Materials. Specific ionic liquids, once immobilized as cations in a polymer structure, allowed for the development of anion ion exchange membranes with the properties required in developing new and efficient electrochemical processes in the conversion of CO₂ to chemicals and fuels. Two new electrochemical processes were developed using these Sustainion[®] anion membranes. The first process was the electrochemical reduction of CO₂ to CO. The second process was the direct reduction of CO₂ that could directly produce a concentrated pure formic acid product. Researchers have been reporting some excellent electrolyzer performance results using these new Sustainion[®] anion membranes, with some of this data tabulated in this paper.

Author Contributions: J.J.K., Z.L., H.Y., S.D.S. and R.I.M. all fully contributed to the information and analysis provided in this review paper as well as in the writing and editing of this manuscript. H.Y. provided the new formic acid cell data and Z.L. the new CO₂ cell data. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors have submitted patents on the membranes and cell designs used for the work here, including U.S. 9,370,773, U.S. 9,481,939, U.S. 9,580,824, U.S. 9,815,021, U.S. 9,982,353, and U.S. 9,943,841. The authors and Dioxide Materials have a financial interest in these patents. Dioxide Materials is offering all of the research materials used here (membranes, cells, catalysts, etc.) for sale to other research groups so that they can reproduce results and build on the findings. The authors declare a financial interest in these sales.

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