Supplementary Information

Towards Accelerated Durability Testing Protocols for CO_2 Electrolysis

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I. Standard Durability Testing in an MEA-based Electrolyzer

The benchmark durability test was performed using a commercial MEA-based electrolyzer (Dioxide Materials). The Ag cathode was prepared in house while the IrO_2 anodes was store-bought (Dioxide Materials) with loadings of 4 mg cm^{-2} and 2 mg cm^{-2}, respectively. Stainless steel made up the cathode current collector while titanium was used for the anode current collector. The cell was assembled using a polytetrafluoroethylene (PTFE) gaskets for both the cathode and anode. A Sustainion membrane (X37-50RT, Dioxide Materials) was placed between the electrodes to create the MEA, and the entire cell was clamped using 10 screws (4 metal and 6 plastic) to 4 N•m with a torque wrench to allow for even pressure distribution.

An insulated monkey clip held the cell vertically. CO_2 was bubbled at 17.5 mL min^{-1} *via* mass flow controller (Brooks, SLA5850) through a water bath (25ºC) to humidify the stream and then to the cell. 0.1 M $KHCO_3$ kept in jacketed collection vessel was constantly fed to the anode using a peristaltic pump (VWR, PP3300D) recycled through the cell. The cell was hooked up to a potentiostat (Autolab, PGSTAT302N) used to supply current and record the corresponding cell and cathode (against a Ag/AgCl reference electrode, ALS, RE-3VT) potentials. The reference electrode was placed downstream of the electrolyte peristaltic pump, close to the cell. Once everything was connected and flowing, the cell was maintained at open current potential for 15 minutes before applying the current. Gas chromatograph (Interscience, CompactGC$^{4.0}$) injections were taken every 2 hours to later calculate Faradaic efficiency, CO_2 conversion, and CO_2 crossover.

II. Durability Testing in an Alkaline Flow Electrolyzer

A. Electrode Preparation

All catalysts were deposited on a gas diffusion layer (GDL, Sigracet 39BC, Fuel Cell Store) to create a gas diffusion electrode (GDE). Commercial Ag NP (Sigma Aldrich, <100 nm, 99.5%) and IrO_2 NP (non-hydrate, Alfa Aesar) were airbrushed onto the GDLs using a setup described previously.[1, 2] To create an ink, the catalyst powder, DI water, Nafion® solution (5wt%, Fuel Cell Earth), and isopropanol were added to a vial. The mixture was then sonicated in a water bath for 20 minutes to create a dispersion before being applied to the GDL *via* airbrush. The final loadings of the Ag cathodes were 1.0 ± 0.1 mg cm^{-2} or 0.5 ± 0.05 mg cm^{-2}. The final loading of the IrO_2 anodes was 1.0 ± 0.1 mg cm^{-2}. A fresh electrode was used for each experiment.

B. Material Characterization

Scanning electron microscopy images were taken of the Ag cathodes before and after testing using the JEOL 7000F. The acceleration voltage was 15.0 kV with a working distance of 10 mm.

C. Accelerated Durability Testing

Accelerated durability testing was performed with a custom gas diffusion electrode-based flow electrolyzer hooked up to a potentiostat (Autolab PGSTAT-30) to conduct chronopotentiometry experiments that applied current and measured resulting cell potential.[2, 3] Stainless steel plates served as current collectors to hold the flow cell together *via* a squeeze-action toggle plier clamp (McMaster Carr) and provided electrical contact between the GDEs and the potentiostat. The cathode and anode potentials were measured using multimeters (Crenova, MS8233D) against a Ag/AgCl reference electrode (Basi, RE-5B). A polyether ether ketone (PEEK) spacer was used for the electrolyte flow. All tests were completed with a KOH (Sigma Aldrich, 99.99%) electrolyte flowing at 0.5 mL min^{-1} and with a CO_2 flow rate of 17 SCCM. Products of the reduction were analyzed to determine the activity (partial current density) and the Faradaic efficiency of the catalyst. The gaseous product stream was fed directly to a gas chromatograph (Thermo Finnigan Trace GC) furnished with a thermal conductivity detector.

Table S1 Comparison between the characteristics of accelerated durability testing (ADT) and accelerated stress testing (AST) methods[4]

Characteristic	Accelerated Durability Testing	Accelerated Stress Testing
Shortened test length	✓	✓
System under stressful environment during operation		✓
Extreme values of typical operating conditions	✓	
Assumption of similar failure mechanisms as standard durability		✓
Defining long term failure mechanisms	✓	

Table S2. Standard operating procedure for running an ECO_2RR durability test to benchmark a cell configuration prior to beginning ADT studies

Cell Configuration and Materials		**Operating Conditions**	
Cell Type	MEA	Cathode Feed:	100% CO_2
Gas Diffusion Layer:	Sigracet 31BC[i]	Relative Humidity:	100%
Catalyst Deposition:	Spray-coating	F_{CO2}:	17.5 mL min^{-1}
Cathode Catalyst:	2 mg cm^{-2} Ag NP w/ 2-4 wt% Sustainion binder	P_{CO2}:	10 psig[ii]
Anode Catalyst:	IrO_2	$F_{electrolyte}$:	1 mL min^{-1}
Catholyte:	N/A	Catholyte Recycling:	N/A
Anolyte:	0.1 M $KHCO_3$	Anolyte Recycling:	Yes
Membrane:	Sustainion 37-50 AEM	Temperature:	25°C
		Pressure:	1 atm
		Applied Current Density:	–200 mA cm^{-2}

Pre-testing Characterization and Preparation

1. SEM EDS/EDX. Take SEM images of the entire cathode at least from a top view. The voltage may vary, but use magnifications around 25x, 1000x, and 10,000x to obtain pictures of the catalyst layer as a whole along with layer morphology. At the median magnification, collect an EDS/EDX map of the cathode surface.
2. Solid State XRF. Measure XRF of the cathode to collect information on catalyst layer composition as a reference for post-test characterization.
3. Prepare Electrolyte. Dissolve enough electrolyte salt in deionized (>18 mΩ-cm) water to get at least 250 mL of electrolyte and cool to room temperature before continuing.
4. Electrolyte XRF. Measure XRF of the electrolyte to check the electrolyte for impurities and to obtain a reference for post-test characterization.

Pre-testing Conditioning and Preparation

5. Soak Membrane. If using a membrane, be sure it has been properly conditioned prior to use. The anion exchange membrane should be soaked in 1 M KOH for at least 24 h.
6. Electrode Conditioning. Soak cathode in 1 M KOH for 1 h to exchange Cl^- ions in Sustainion with OH^-
7. Assemble Cell. Put cell together using cathode, anode, membrane, gasket(s), flow chambers, current collectors, and tubing.

Pre-testing Electrochemical Conditioning

8. LSV (if using easily oxidized catalyst). Run an LSV from 0 to –0.40 V vs RHE to get rid of any oxides that might be present in the catalyst layer.

Pre-testing Electrochemical Characterization

10. Potentiostatic EIS. Conduct an EIS experiment to measure cell and charge resistance. Set the cathode potential to –0.25 V vs RHE and the frequency range at 10 kHz to 0.1 Hz.

Durability Test

11. Begin applying the current.
12. Wait for the cell potential to equilibrate and for effluent gas to fill volume from cell through GC.
13. Take the first GC injection. This marks *t*=0. Ensure the FE of the main product is at expected value.
14. Set GC to take an injection every hour or manually take injection every hour while applying potential for a total of 50 h. Collect individual electrode potential data every hour as well, if possible.
15. Stop applying the current, but **do not** disassemble cell or disconnect

Post-testing Electrochemical Characterization

16. Potentiostatic EIS. Conduct an EIS experiment to measure cell and charge resistance. Set the cathode potential to –0.25 V vs RHE and the frequency range at 10 kHz to 0.1 Hz. Afterwards, disassemble cell being careful not damage the cathode.

Post-testing Characterization

18. SEM EDS/EDX. Take SEM images of the entire electrode at least from a top view. Be sure to use the same conditions and magnifications as the initial SEM images. At the median magnification, collect an EDS/EDX map of the cathode surface.
19. Solid State XRF. Measure XRF of the electrode using the same conditions as the pre-testing measurements.
20. Electrolyte XRF. Measure XRF of the electrolyte using the same conditions as the pre-testing measurements.
21. Mass Balance. Using GC data from the entire testing period, complete carbon mass balances to determine CO_2 crossover across the membrane and CO_2 conversion at the cathode

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[i] Sigracet 31BC has since been discontinued and has been replaced with 39BB in our experiments

[ii] CO_2 pressure can range; should represent value needed to maintain proper pressure balance within cell

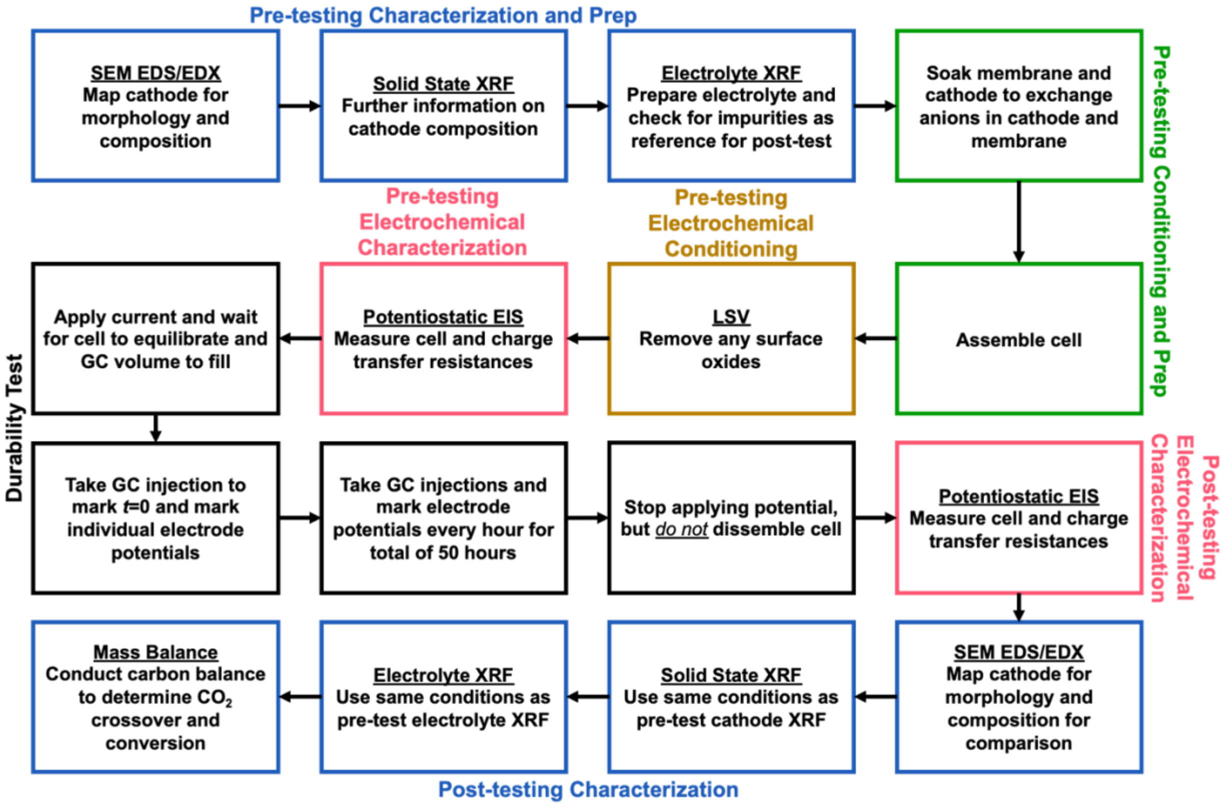

Figure S1 Flow chart of the steps for the benchmark standard durability test

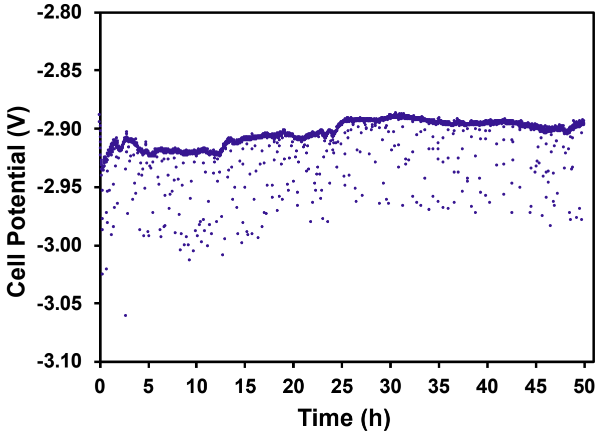

Figure S2 Complete cell potential graph over the duration of the benchmark ECO$_2$RR durability test conducted in the MEA-based cell configuration

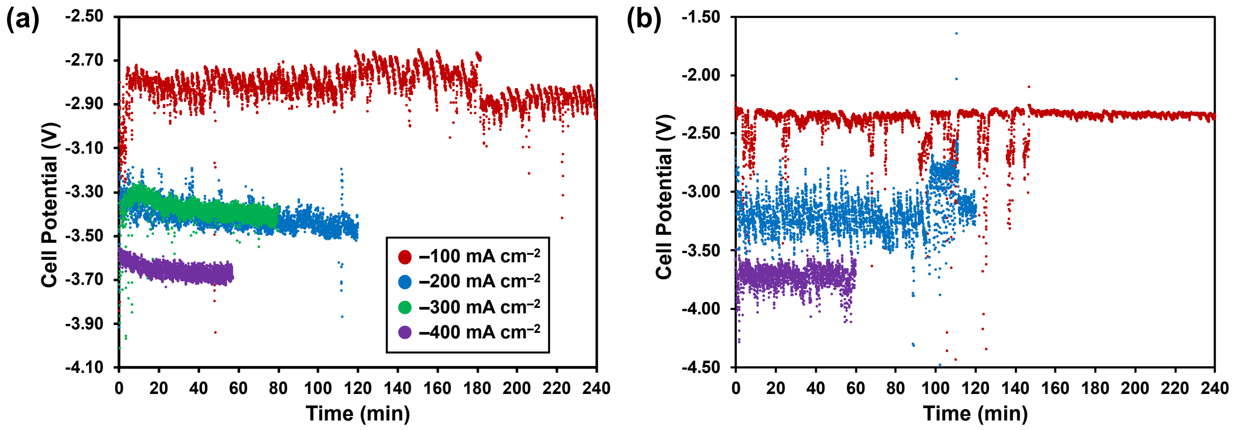

Figure S3 Complete graphs of cell potential over the duration of the charged passed ECO_2RR accelerated tests conducted in an alkaline flow electrolyzer. (a) 0.5 mg cm^{-2} Ag NP cathode (b) 1.0 mg cm^{-2} Ag NP cathode. The legend is the same for both graphs. The absolute value of the cell potential increases as higher currents are applied.

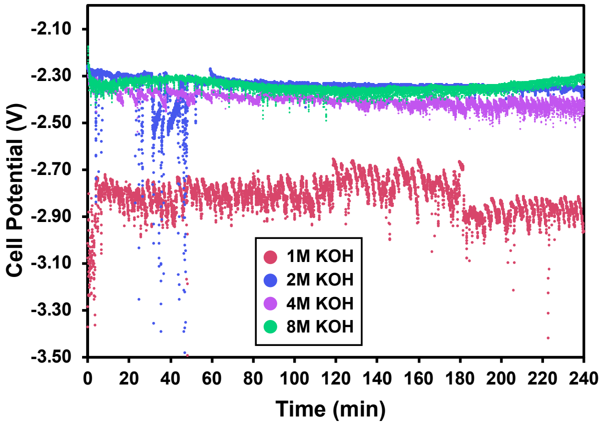

Figure S4 Complete graphs of cell potential over the duration of the electrolyte molarity ECO_2RR accelerated tests conducted in an alkaline flow electrolyzer. The absolute value of the cell potential decreases when changing from 1M to 2M KOH but remains the same when increasing the morality further.

Table S3 The rate degradation in FE_{CO} for each applied current density in the total charged passed ECO_2RR acceleration tests conducted in an alkaline flow electrolyzer. The rate of degradation is the slope of the linear fit for the FE plot.

Applied Current Density ($mA\ cm^{-2}$)	Degradation Rate ($\%\ min^{-1}$)
–100	0.01700
–200	0.04900
–300	0.10500
–400	0.32600

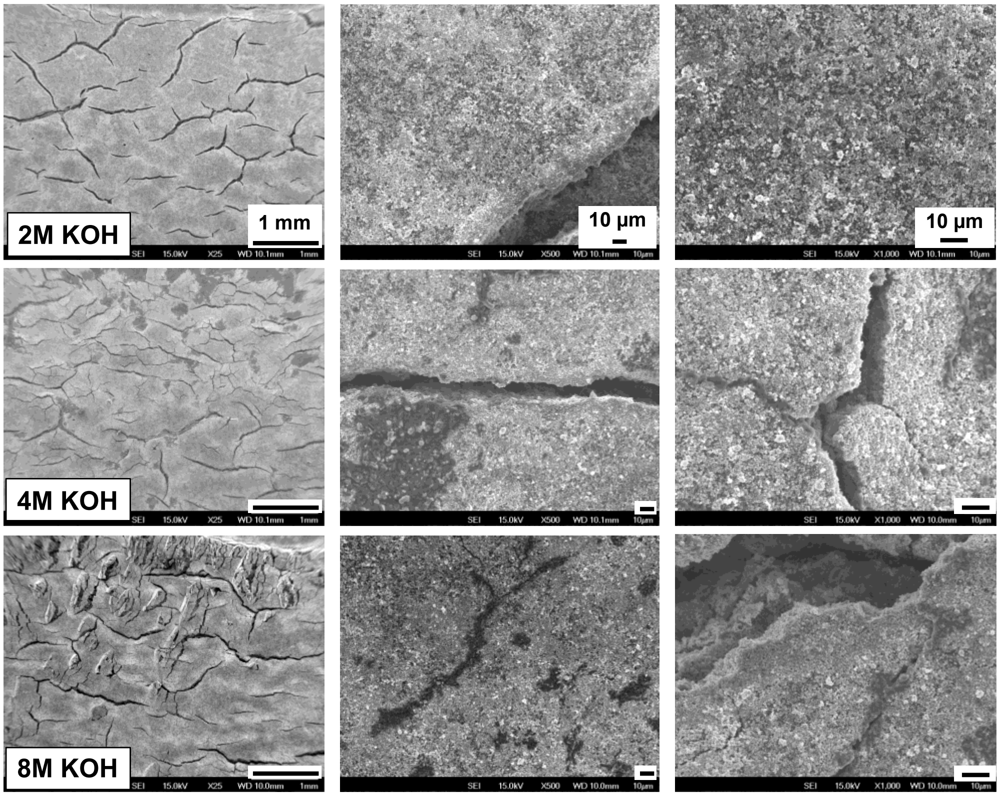

Figure S5 SEM images of the 0.5 mg cm^{-2} Ag NP taken after each of the electrolyte molarity accelerated ECO_2RR tests conducted in an alkaline flow cell. As the electrolyte (KOH) molarity increases, carbonate (darker patches) forms on the catalyst layer. In addition, the catalyst layer begins to detach from the carbon substrate, signaling the onset of Ag leaching, most notability with the 8M KOH experiment.

References

1. S. Ma, J. F. Liu, K. Sasaki, S. M. Lyth and P. J. A. Kenis, *Energy Technol-Ger*, 2017, **5**, 861-863.
2. H. R. Jhong, C. E. Tornow, C. Kim, S. Verma, J. L. Oberst, P. S. Anderson, A. A. Gewirth, T. Fujigaya, N. Nakashima and P. J. A. Kenis, *Chemphyschem*, 2017, **18**, 3274-3279.
3. S. Ma, M. Sadakiyo, R. Luo, M. Heima, M. Yamauchi and P. J. A. Kenis, *J Power Sources*, 2016, **301**, 219-228.
4. Fundamentals of Accelerated Stress Testing, https://thermotron.com/wp-content/uploads/2016/02/HC-100-AST-Handbook.pdf, (accessed October 11, 2020).