Supporting information:

Quantifying and Elucidating the effect of CO$_2$ on the Thermodynamics, Kinetics and Charge Transport of AEMFCs

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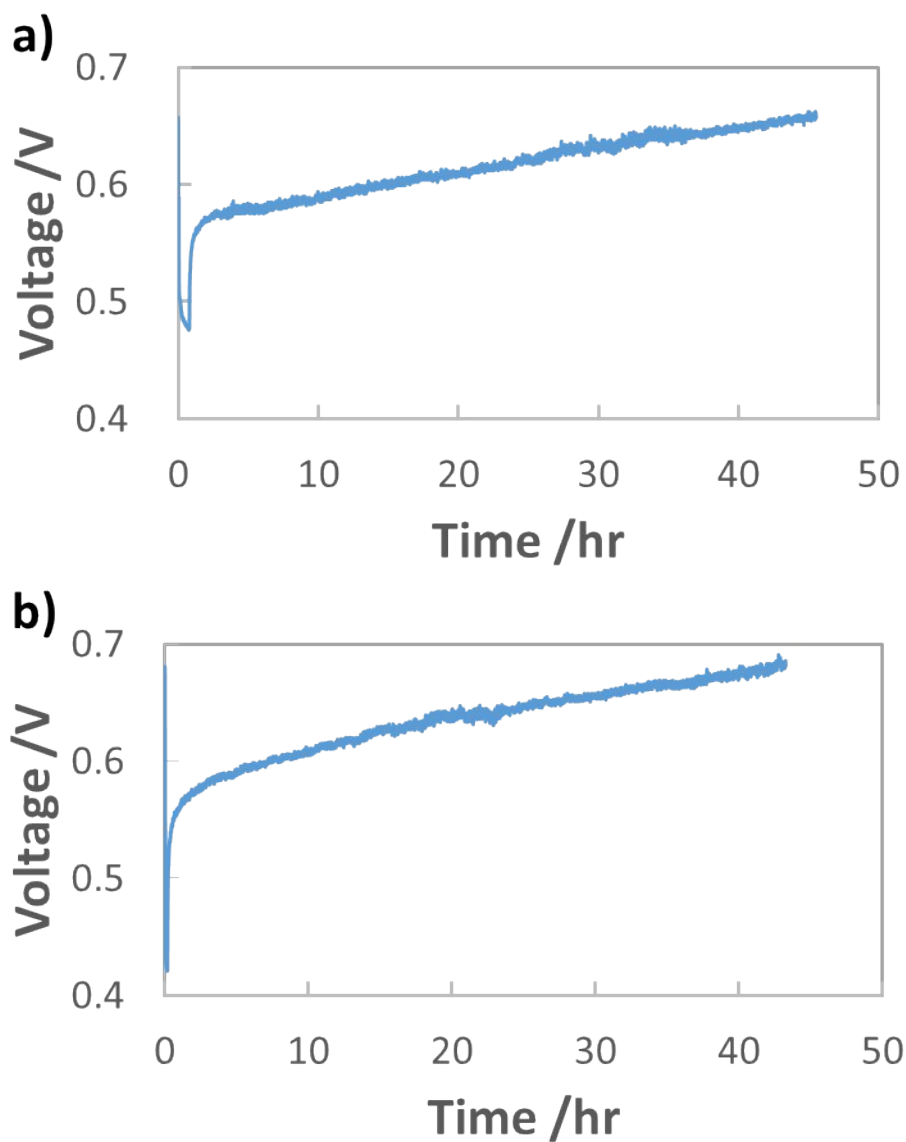[c] National Renewable Energy Laboratory, Golden, Colorado 80401, USA

Figure S1. Voltage recovery from 400 ppm CO_2 exposure when fed to a) anode b) cathode under constant current operation at 1 A cm^{-2}.
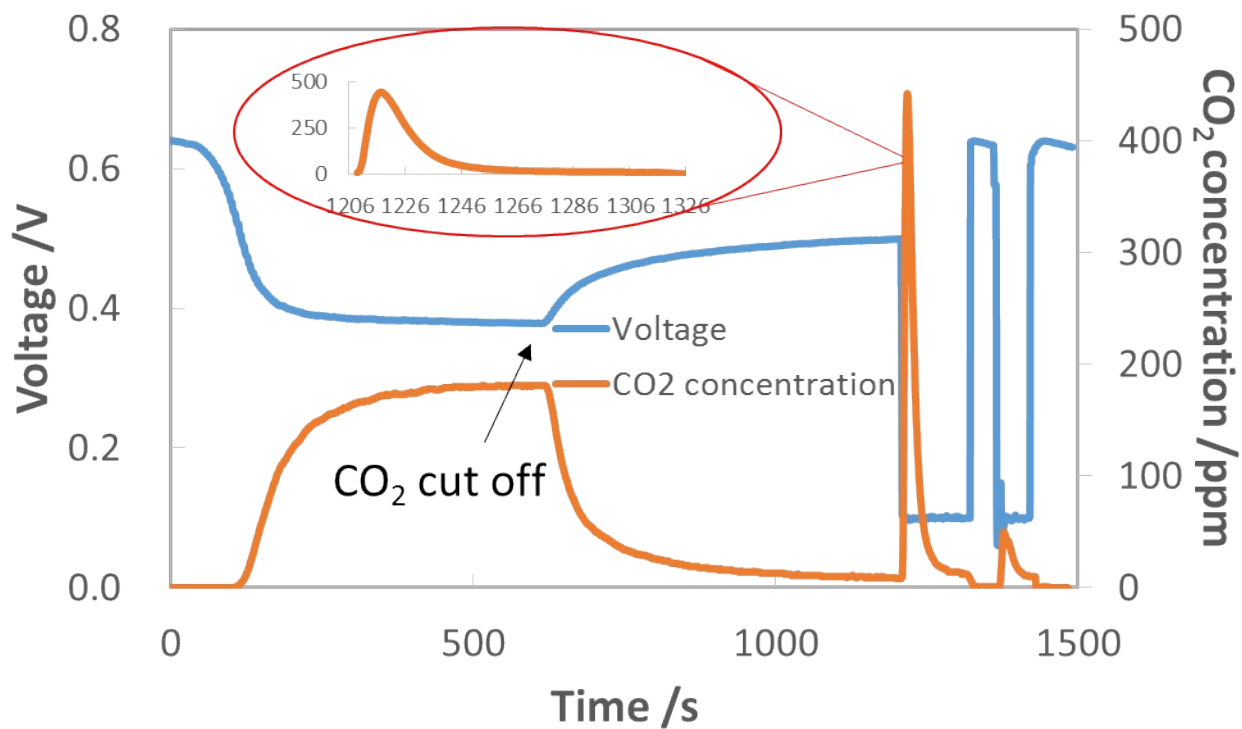
Figure S2. Rapid recovery of AEMFC performance through forced decarbonation by pulsing the operating voltage to 0.1V for 2 min. The concentration of the carbonate that was in the AEMFC can be calculated from the measured transient CO_2 concentration in the anode effluent during the pulse (not shown).
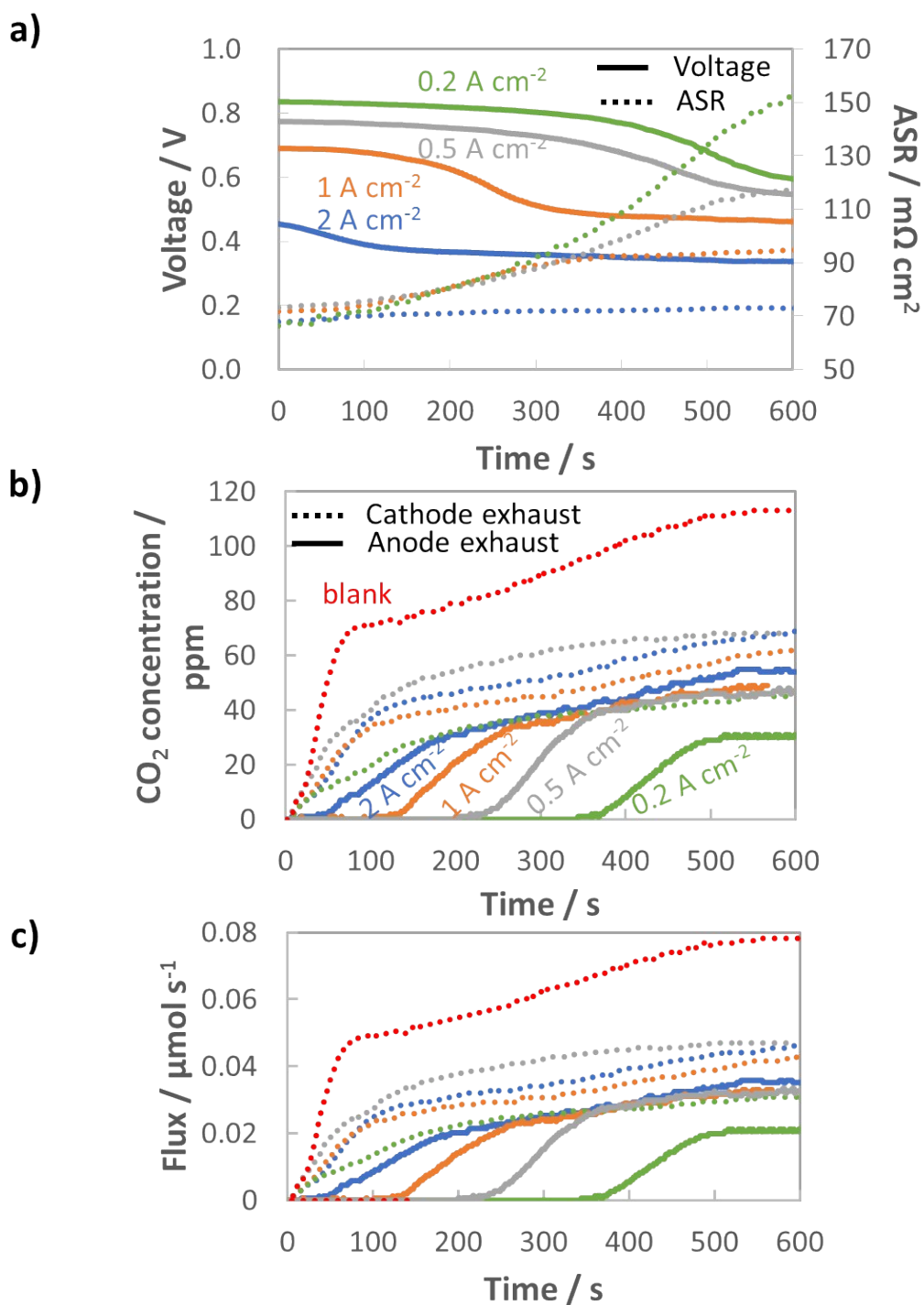
Figure S3. Uptake of 100 ppm CO_2 fed to the cathode of H_2/O_2 AEMFCs operating at 60°C and discharging at 0 (load off), 0.20, 0.50, 1.0 and 2.0 A cm^{-2} current densities. a) voltage decrease and ASR increase upon introduction of CO_2 into the cathode reacting gas; b) CO_2 emission from the anode (solid lines) and cathode (dotted lines) when 100 ppm CO_2 is fed to the cathode; c) CO_2 flux fed to the cell and released from the anode (solid lines) and cathode (dotted lines) when 100 ppm CO_2 is fed to the cathode

Figure S4. Uptake of 200 ppm CO_2 fed to the cathode of H_2/O_2 AEMFCs operating at 60°C and discharging at 0 (load off), 0.20, 0.50, 1.0 and 2.0 A cm^{-2} current densities. a) voltage decrease and ASR increase upon introduction of CO_2 into the cathode reacting gas; b) CO_2 emission from the anode (solid lines) and cathode (dotted lines) when 200 ppm CO_2 is fed to the cathode; c) CO_2 flux fed to the cell and released from the anode (solid lines) and cathode (dotted lines) when 200 ppm CO_2 is fed to the cathode
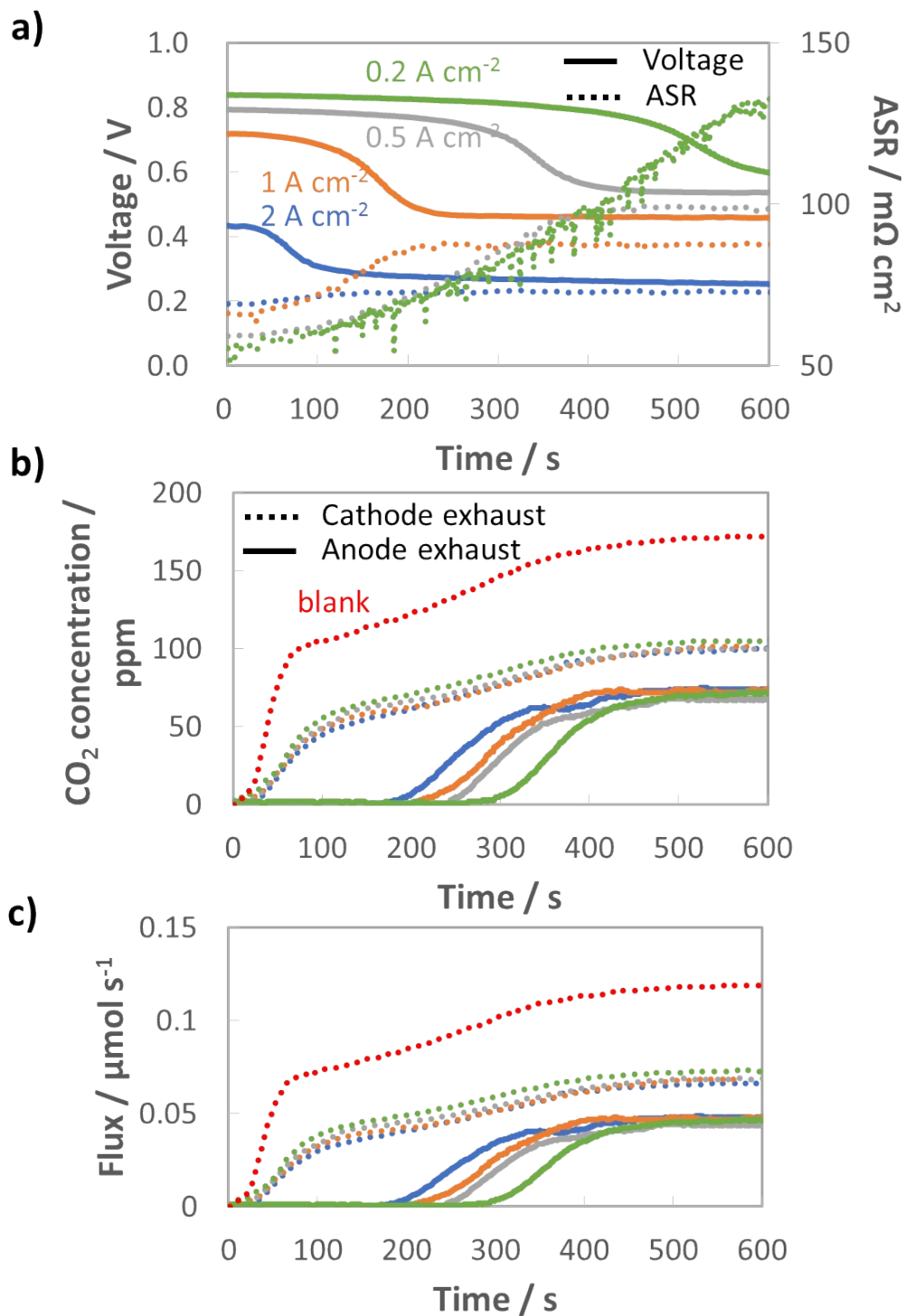
Figure S5. Uptake of 800 ppm CO_2 fed to the cathode of H_2/O_2 AEMFCs operating at 60°C and discharging at 0 (load off), 0.20, 0.50, 1.0 and 2.0 A cm^{-2} current densities.   a) voltage decrease and ASR increase upon introduction of CO_2 into the cathode reacting gas; b) CO_2 emission from the anode (solid lines) and cathode (dotted lines) when 800 ppm CO_2 is fed to the cathode; c) CO_2 flux fed to the cell and released from the anode (solid lines) and cathode (dotted lines) when 800 ppm CO_2 is fed to the cathode
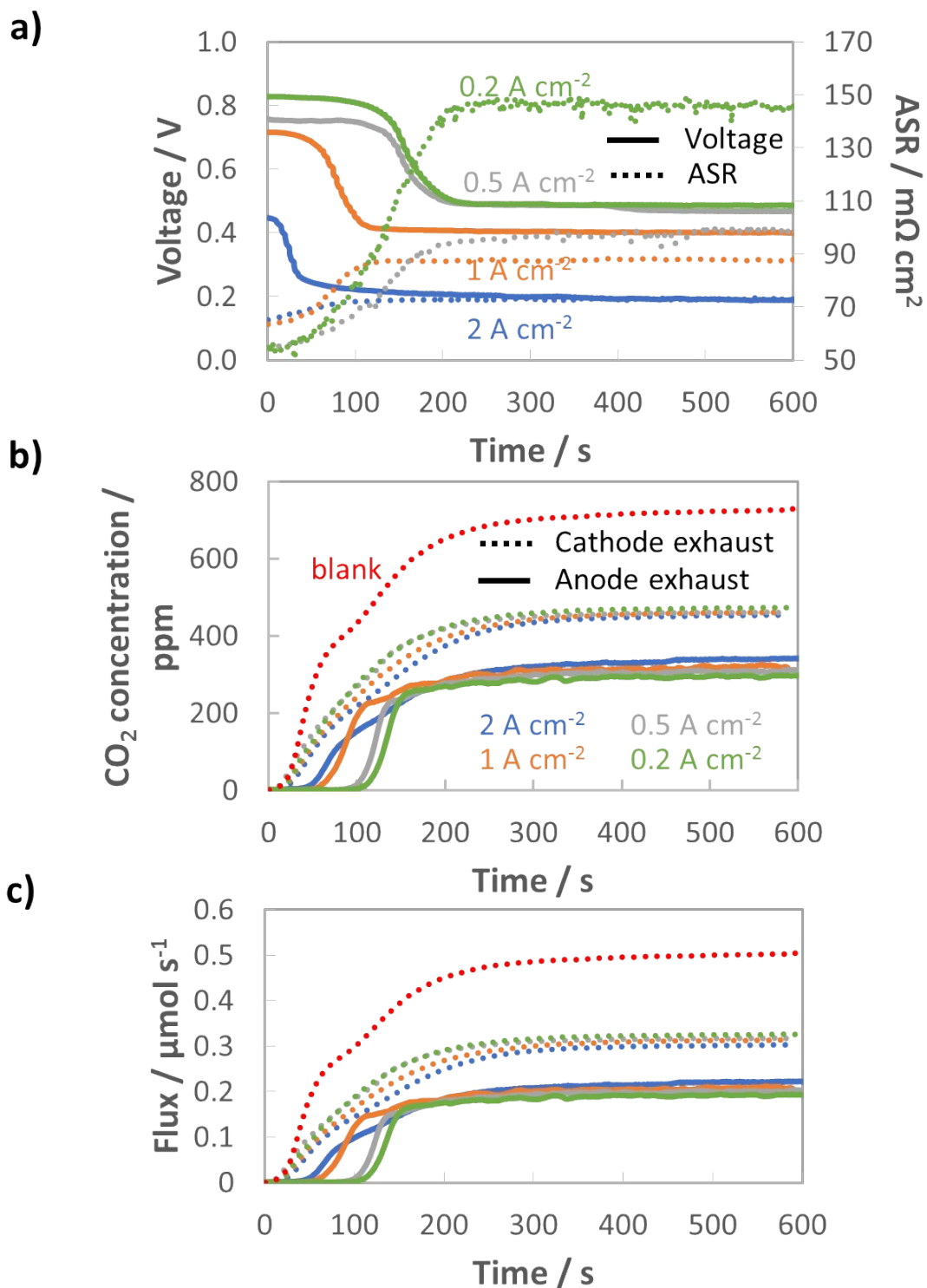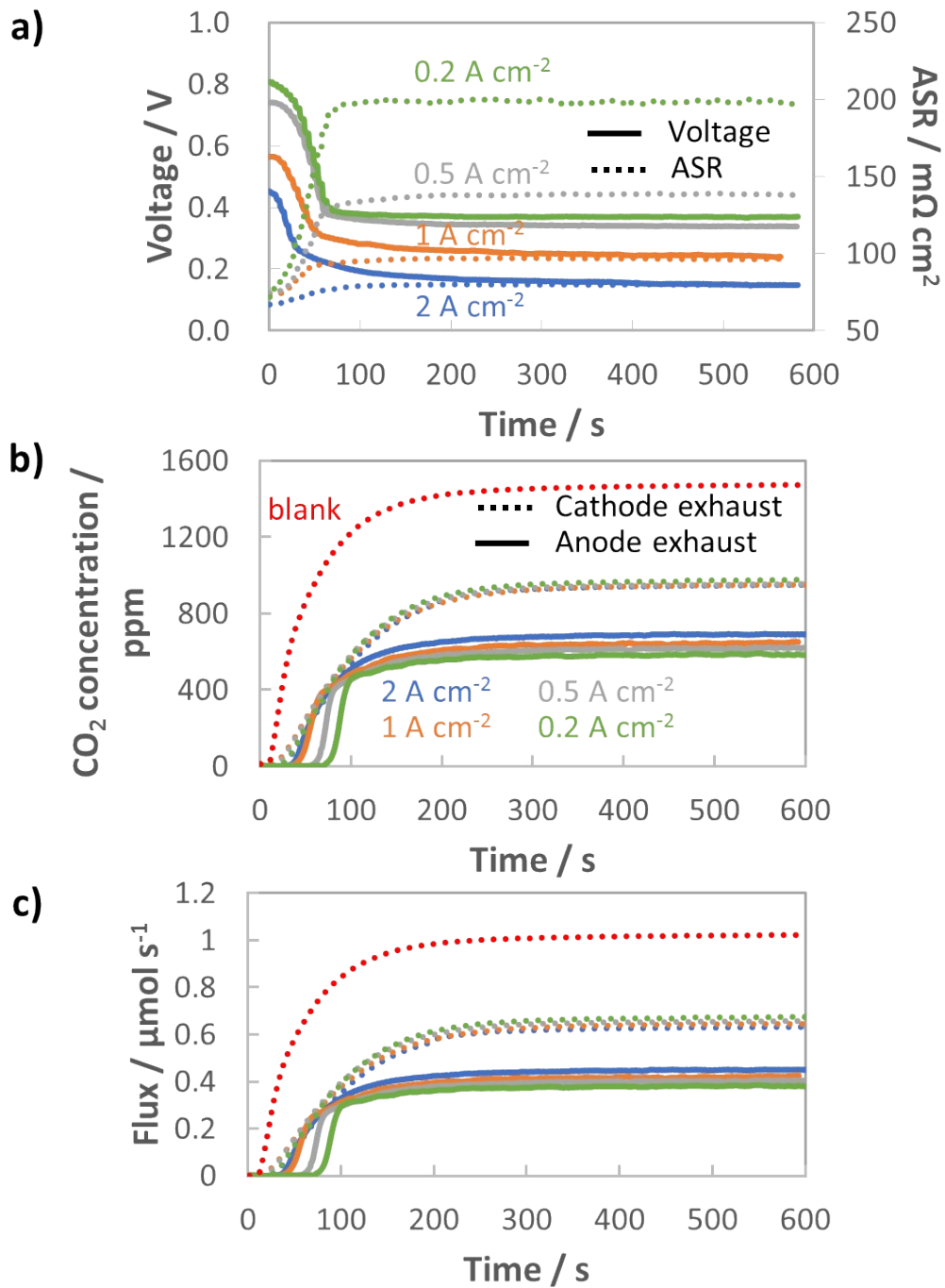
Figure S6. Uptake of 1600 ppm CO_2 fed to the cathode of H_2/O_2 AEMFCs operating at 60°C and discharging at 0 (load off), 0.20, 0.50, 1.0 and 2.0 A cm^{-2} current densities. a) voltage decrease and ASR increase upon introduction of CO_2 into the cathode reacting gas; b) CO_2 emission from the anode (solid lines) and cathode (dotted lines) when 1600 ppm CO_2 is fed to the cathode; c) CO_2 flux fed to the cell and released from the anode (solid lines) and cathode (dotted lines) when 1600 ppm CO_2 is fed to the cathode
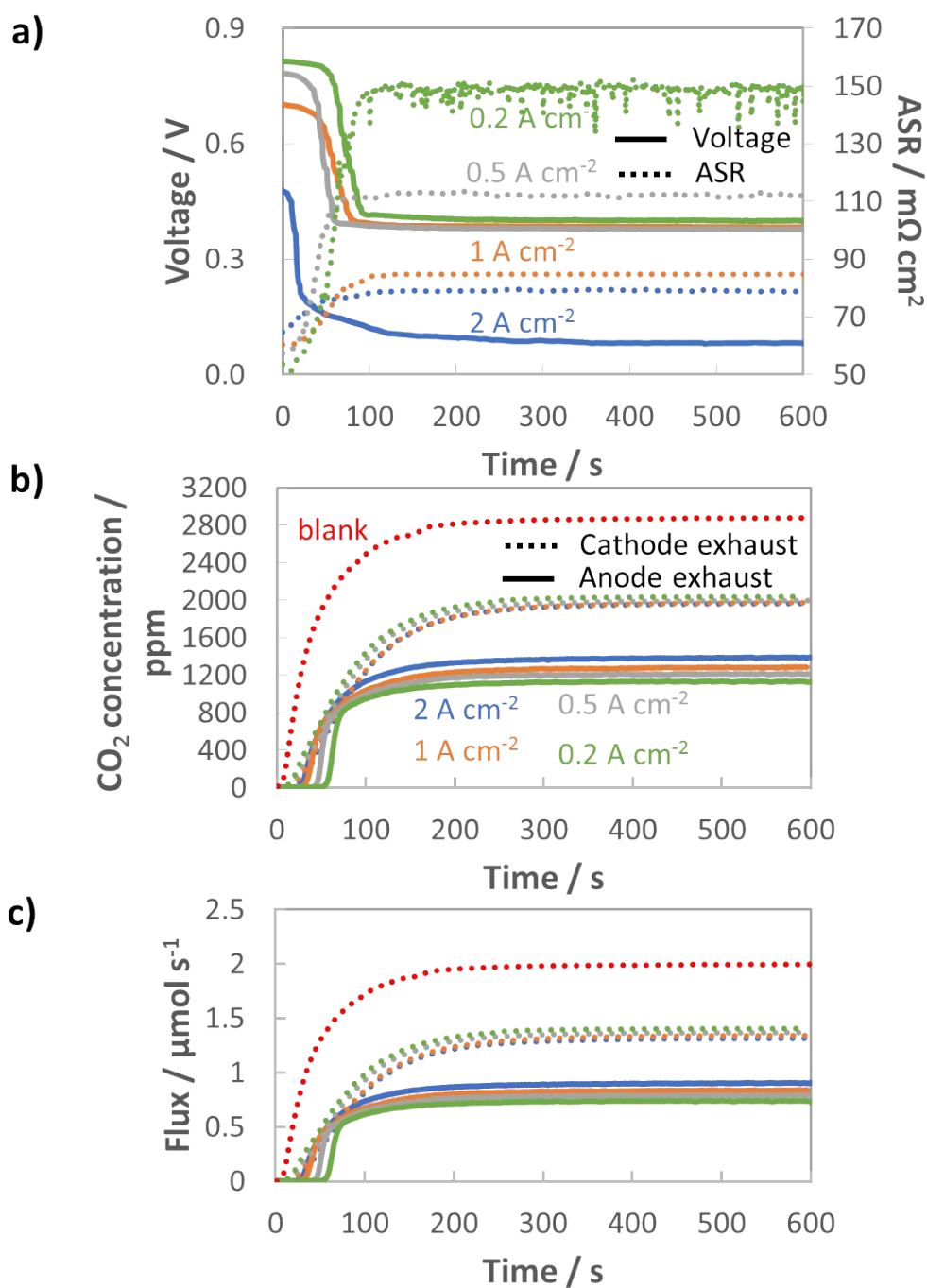
Figure S7. Uptake of 3200 ppm CO_2 fed to the cathode of H_2/O_2 AEMFCs operating at 60°C and discharging at 0 (load off), 0.20, 0.50, 1.0 and 2.0 A cm^{-2} current densities. a) voltage decrease and ASR increase upon introduction of CO_2 into the cathode reacting gas; b) CO_2 emission from the anode (solid lines) and cathode (dotted lines) when 3200 ppm CO_2 is fed to the cathode; c) CO_2 flux fed to the cell and released from the anode (solid lines) and cathode (dotted lines) when 3200 ppm CO_2 is fed to the cathode
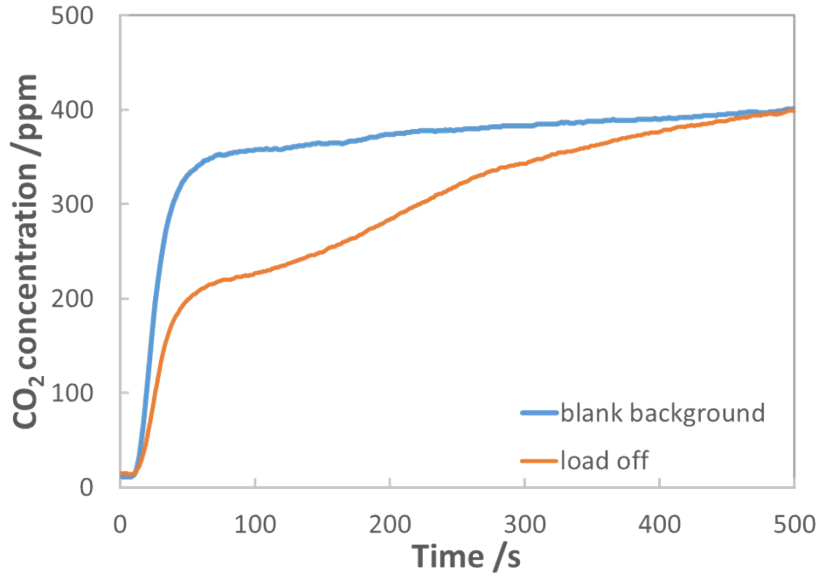
Figure S8. Comparison of CO_2 concentration leaving the AEMFC (fed at 400 PPM) when an AEMFC MEA is present and when Teflon is placed between the flowfields with no electrodes.   Hence, the quantity of CO_2 that has been taken up into the cell by the AEM and AEI is the integrated area between these two plots.   From here, the degree of carbonation (DOC, % of charge groups converted to the carbonate form) can be calculated by:

$$DOC = \frac{(Charge\ per\ CO_2)(\mu mol\ CO_2)}{(Charge\ per\ group)(\mu mol\ AEM\ groups + \mu mol\ AEI\ groups)} = \frac{(2)(38.2)}{(1)(42.8 + 25.5)} = 1.11 = 111\%$$

This number being higher than 100% validates literature data on membranes that were carbonated outside of operating cells with no current flowing where the balance in the membrane is a mixture of both carbonate and bicarbonate.   We could use the data above to make a rough calculation of the ratio of carbonate to bicarbonate since bicarbonate cannot exist with significant quantities of OH^- and CO_3^{2-} due to the equilibrium constraints.

If it is assumed that the ionomeric materials are completely carbonated, then the average charge per CO_2, ε, can be found by:

$$\frac{(\varepsilon)(38.2)}{(42.8 + 25.5)} = 1.00$$

Here, $\varepsilon = 1.79$, meaning that 79% of the charge groups are in the CO_3^{2-} form and 21% are in the HCO_3^- form at open circuit.

Table S1. Degree of carbonation of operating AEMFCs (AEM+AEI) as a function of current density and CO_2 concentration in the cathode

Current Density (A cm^{-2})	PPM CO_2 in Cathode	Carbonate in AEMFC (umol) during CO_2 exposure	DOC during CO_2 exposure (%)	Carbonate remaining in AEMFC (umol) after CO_2 removed, @ new quasi steady state	DOC, after CO_2 removed, and new quasi steady state established after ~ 10 min (%)
2.0	400	13.5	39.5	5.7	16.6
1.0	100	4.7	13.9	7.9	~22
	200	11.1	32.4	8.1	
	400	18.0	52.8	7.2	
	800	28.1	82.2	6.9	
	1600	38.8	113	7.9	
0.5	100	20.7	60.1	10.3	30.0
0.2	100	25.4	74.4	14.4	41.9
0.0 (no current)	400	38.2	111	N/A	N/A

To calculate the quantity of carbonate anions in the operating cell at steady state for any operating condition, we only need to be able to quantify the number of CO_2 molecules that were taken up by the cell. The data in Figure 2c and Figures S3c-S7c provide a pathway to do this because it gives the molar flux of CO_2 that is entering the cell when no uptake occurs ("blank"). It also provides the CO_2 flux that is leaving from both the anode and cathode with time until the cell reaches steady state. From this data, the three curves ("blank" vs. time, anode exhaust vs. time, and cathode exhaust vs. time) can be integrated and the total number of moles of CO_2 (N_{CO2}), and hence CO_3^{2-}, can be calculated by:

$$N_{CO2} = \int "blank"(t)\, dt \; - \int "anode\ exhaust"(t)\, dt \; - \int "cathode\ exhaust"(t)\, dt$$

From here, the DOC was also calculated from the equation above.

Another interesting point in the dataset where it would be informative to know how much carbonate was in the system is after the CO_2 was removed from the cathode and the cell has reached the new quasi steady state. In the main manuscript, Figure 4a showed a set of typical carbonation + decarbonation experiments, where the cell was exposed to a known amount of CO_2 for 30 min and then the CO_2 was removed from the cathode gas stream. Cell decarbonation happened in 2 stages. The first stage was when we operated the cell for 30 min at the same current density. The second stage occurred after this 30 min of operation, when we pulsed cell down to 0.1 V. Here, the CO_2 coming out of the anode came out in a large slug that quickly decayed over 1-2 minutes. After that, the cell voltage was allowed to come back to steady state at the initial operating current and "complete" decarbonation was assumed if the steady state voltage was equal to the pre-CO_2 exposed operating voltage. The amount of carbonate left after the ~10 min new quasi steady state can be found by integrating the area

under the slug of CO_2 that was measured with time at 0.1V.   This calculation was also done for every current density and cathode CO_2 concentration and the resulting values are tabulated in Table S1.   From here, the DOC was calculated from the equation above.
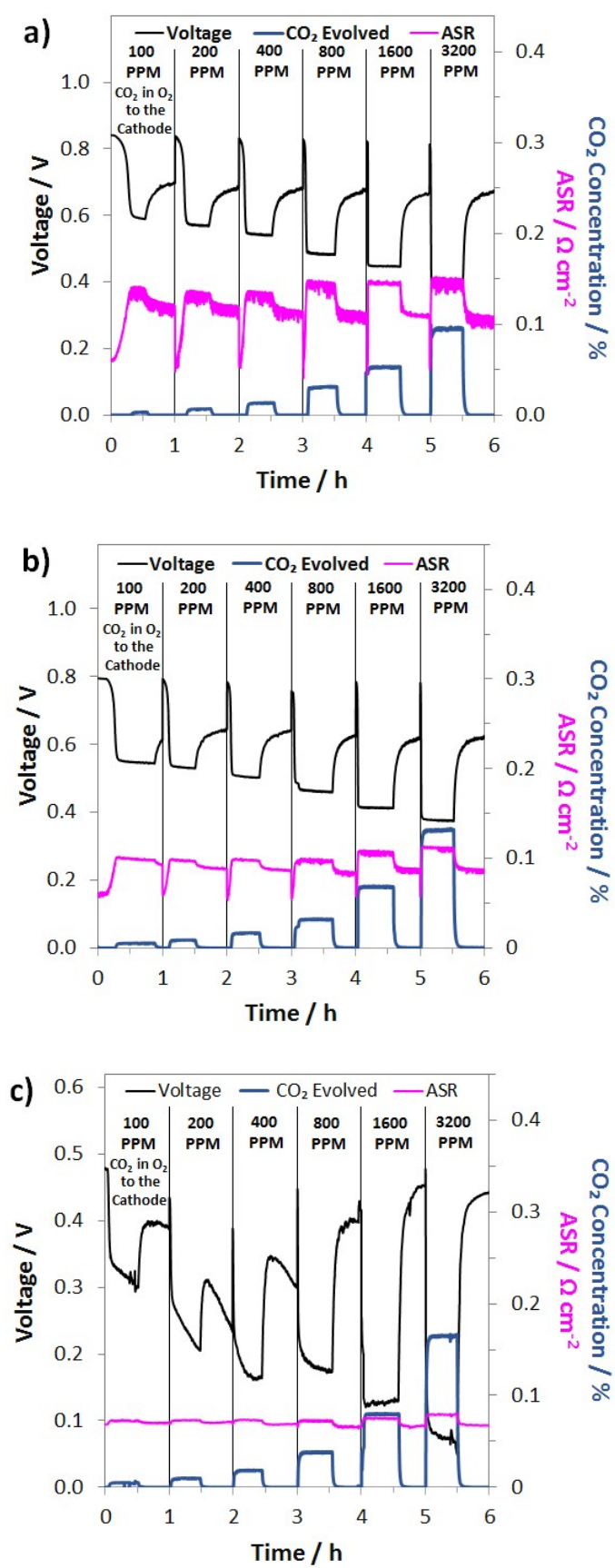
Figure S9. Response of an AEMFC operating at a) 0.2, b) 0.5 and c) 2.0 A cm^{-2} to various concentrations of CO$_2$ in the cathode reacting gas

Table S2. Summary of the CO_2-related resistances and overpotentials as a function of current density and cathode CO_2 concentration (in O_2). The AEMFC was operated at 60°C with an ETFE-BTMA AEM. Gas flowrates were 1 L min-1 at both the cathode and anode (H_2).

Current Density (A/cm²)	PPM CO_2 in Cathode	Total CO_2-related overpotential (mV)	ΔASR (mΩ cm²)	R_{ctHOR} (mΩ)	ΔV_{Ohmic} (mV)	ΔV_{Nernst} (mV)	ΔV_{ctHOR} (mV)
2.0	100	167	6.7	5.3	13.4	101	53
	200	216	8.6	7.3	17.3	125	73
	400	259	9.9	11.3	19.8	126	113
	800	298	11.2	15.2	22.4	123	152
	1600	338	12.9	19.0	25.9	122	190
	3200	385	14.9	22.5	29.9	130	225
1.0	100	236	19.3	10.7	19.3	163	53
	200	246	22.5	12.8	22.5	159	64
	400	281	25.3	18.7	25.3	162	94
	800	319	27.9	25.6	27.9	163	128
	1600	359	32.1	32.8	32.1	163	164
	3200	406	37.5	39.2	37.5	173	196
0.5	100	227	44.2	18.0	22.1	160	45
	200	260	44.4	27.6	22.2	168	69
	400	306	50.4	49.5	25.2	157	124
	800	351	55.8	65.5	27.9	159	164
	1600	394	64.5	82.9	32.3	155	207
	3200	450	72.4	101.7	36.2	159	254
0.2	100	255	88.6	64.1	17.7	173	64
	200	271	88.4	87.0	17.7	167	87
	400	324	98.3	143.2	19.7	161	143
	800	386	116.0	189.0	23.2	173	189
	1600	433	126.6	236.4	25.3	171	236
	3200	486	138.8	278.3	27.8	180	278

Table S3. Calculated values for *ΔASR*, *ΔV*_{Nernst} and *R*_{ctHOR} as a function of operating temperature for AEMFCs operating at a constant current of 1 A cm^{-2} and constant cathode CO_2 concentration of 400 PPM. It should be noted that the membrane here was LDPE-BTMA, so the absolute values can't really be compared with Table S2, but can be inter-compared to determine the impact of temperature on the behavior.

Temperature (ºC)	ΔASR (mΩ cm^2)	ΔV_{Ohmic} (mV)	ΔV_{Nernst} (mV)	R_{ctHOR} (Ω)	V_{ctHOR} (mV)
60	22.6	22.6	226	17.0	84.8
65	17.6	17.6	177	18.0	90.2
70	16.9	16.9	150	18.2	91.1
75	18.2	18.2	134	17.7	88.5
80	15.9	15.9	113	17.2	85.9

Table S4. Degree of carbonation (AEM+AEI) as a function of temperature for AEMFCs with LDPE AEM operating at 1 A cm^{-2} and constant cathode CO_2 concentration of 400 PPM.

Temperature (℃)	60	65	70	75	80
Carbonate in AEMFC (μmol)	17.87	12.44	12.41	11.51	11.37
Degree of Carbonation, DOC (%)	33.98	23.66	23.60	21.88	21.61