Chlorine-induced degradation in SOFCs operating with biogas.

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Electronic supplementary information (ESI)

Information in this document contains figures that support claims made in the body of the submitted manuscript.

Catalytic activity following removal of Cl from incident fuel.

This figure shows the time dependent growth of the graphite 'G' feature in the Raman spectra from Ni-YSZ anodes exposed to biogas at 650˚C and held at open circuit voltage at the start of a 'cycle' in the cycling experiments.

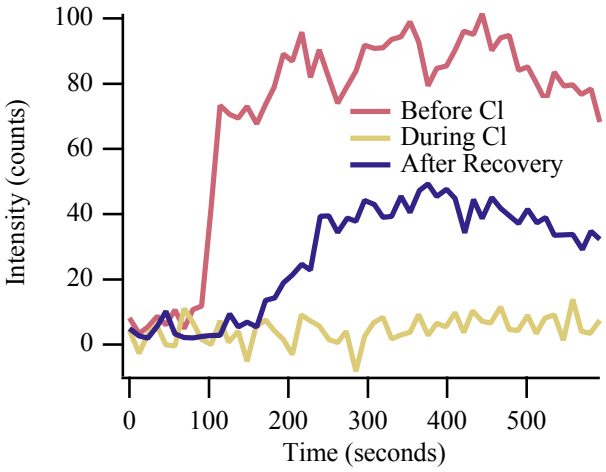

Figure S1: Recovery of the carbon "G" peak after recovery of a fuel cell poisoned by chlorine at 650 °C.

As noted in the manuscript and elsewhere in the literature, Ni-based anodes exposed to biogas at these temperatures show direct evidence of graphitic carbon accumulation. (Figure 2 in manuscript.) This result can be seen in the red 'Before Cl' trace in the figure above. Including 110 ppm chlorine in the biogas (in the form of chloromethane) rapidly suppresses biogas activation and carbon formation. (Yellow 'During Cl' trace.) With biogas at 650˚C and 700˚C, complete suppression of catalyst activity requires less than 30 minutes. (Figures 3 and 4 in manuscript.) Continued cycling *after* chlorine has been removed from the incident fuel leads to partial recovery of catalytic activity as evidenced by the reappearance of the graphite G peak. (Blue, after recovery trace.)

Comparing electrochemical performance of SOFCs operating with biogas and H_2 at 700˚C.

The manuscript contains direct electrochemical comparison between cell operating with hydrogen (H_2) and biogas at 650˚C. (Figures 4 and 5) Similar behavior is observed for each fuel in SOFCs operating at 700˚C as evidenced by the impedance and voltammetry data shown below.

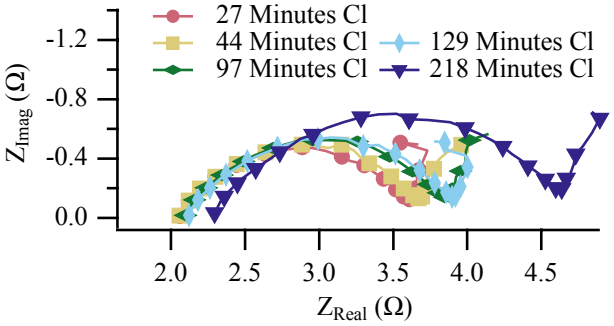

Figure S2: Hydrogen EIS spectra of cell operating at 700 °C.

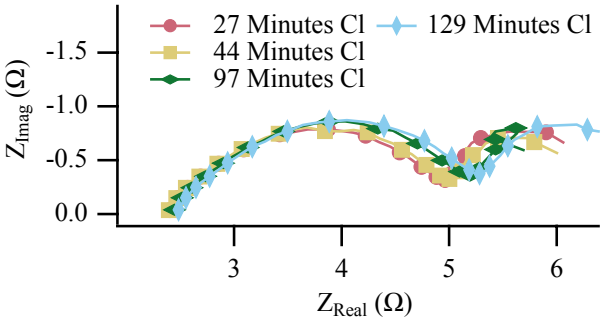

Figure S3: Biogas EIS spectra of cell operating at 700 °C.

EIS data from the SOFC operating with H_2 at 700˚C shows evidence of modest degradation over the span of 218 minutes. This degradation takes the form of a slowly increasing polarization resistance and a series resistance that changes discontinuously between 129 minutes and 218 minutes. This discontinuous change is also noted in the voltammetry data shown below. (Figure S4) These H_2 data are not dissimilar from the 650˚C data presented in Figure 4 in the manuscript. Figure 3 shows EIS data from an SOFC operating with biogas at 700˚C. Again, the data show very modest evidence of cell degradation but no harbinger of the catastrophic failure that is observed in the voltammetry data acquired at 218 minutes. (Figure S5)

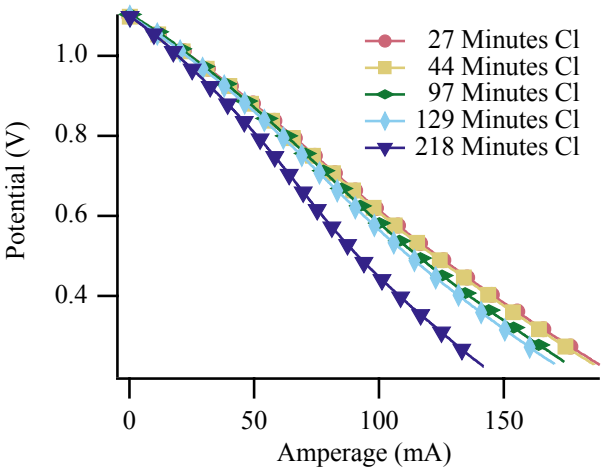

Figure S4: Hydrogen LSV of a cell operating at 700 °C.

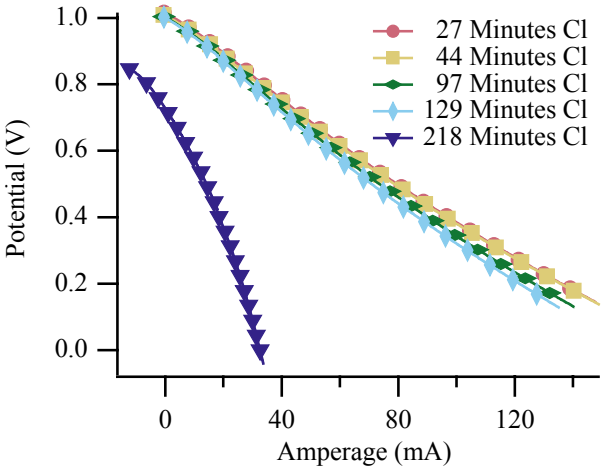

Figure S5: Biogas LSV of a cell operating at 700 °C.

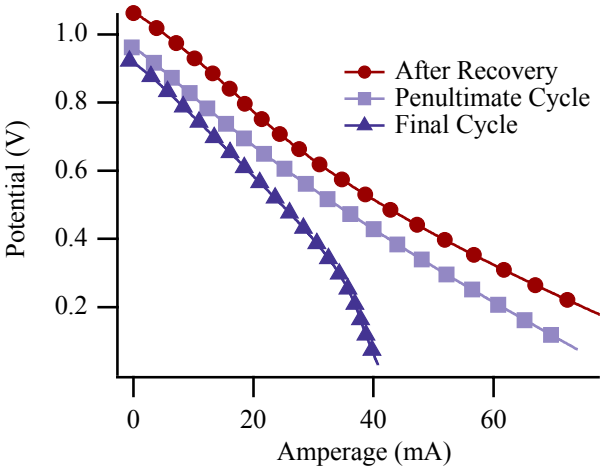

Figure S6: Performance data recovery for a cell operating at 650 °C and recovered for 1 hour in 18 sccm of H_2 with 55 sccm Ar carrier gas after chlorine induced failure. Blue traces above are the final two cycles of chlorine exposure.

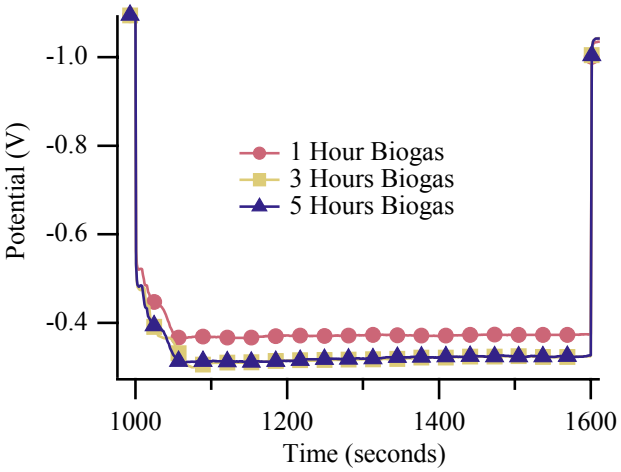

Figure S7: Potential vs. Time plots for a control biogas cycling experiment at 650 °C.

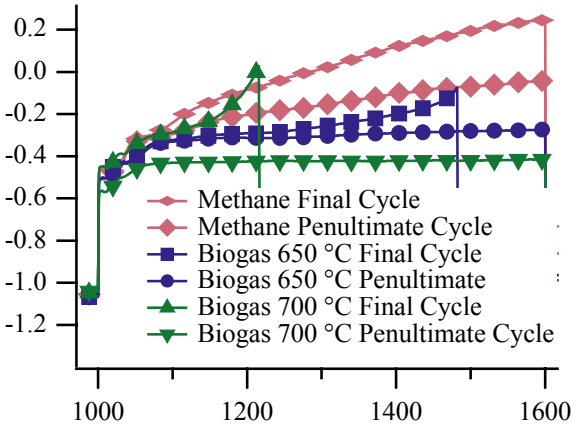

Figure S8: Failure methods for biogas at 650 °C and 700 °C (blue and green respectively) and methane at 650 °C(red). Each set shows the penultimate and final cycle for each experiment.