Study of Current Interruptions in Direct-Methane Solid Oxide Fuel Cells

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The purpose of the summer project was to investigate the effects of repeated current interruptions on solid oxide fuel cells running on methane fuel. Solid oxide fuel cells (SOFCs) are of interest because they could become a widespread technology for stationary power generation, burning natural gas or other hydrocarbons at high efficiency. However, methane, which is the largest constituent of natural gas, has the tendency to result in carbon coking in Ni-YSZ anodes. When operating above a critical current density, the products of the SOFC reaction (namely H_20 and CO_2) are present in quantities substantial enough to shift the thermodynamics away from carbon coking. However, during an interruption of the current, coking is thermodynamically favored, which can result in a permanent decrease in cell performance[1].

In order to test the effects of current interruptions, button cells were processed and characterized. Characterization of the cells was predominantly electrical: performing both AC electrochemical impedance spectroscopy (EIS) and monitoring the current and voltage over time. The conventional Ni-YSZ/YSZ/LSM-YSZ button cell processing will not be detailed here, as a similar procedure has been laid out in papers by the Barnett group[2]. The 7 cells processed for the project had a power density of about 1 W/cm^2 in humidified hydrogen/air at 800°C (before addition of barrier layer). The only major difference in cell production was the addition of a partially-stabilized zirconia (PSZ) barrier layer. PSZ powder (80:20 PSZ:Starch, 0.5wt% PVB binder) was isostatically pressed into pellets with the same diameter as the cell (19 mm), and approximately half (0.4 mm) of the cell thickness (0.7 mm). The barrier layer was placed directly against the anode, and sealed such that the fuel stream was forced to diffuse through it in order to reach the anode. The purpose of the barrier layer is to mitigate coking effects by reducing the partial pressure of fuel at the anode and increasing the partial pressures of H_2O and CO_2. Doing so shifts the thermodynamic equilibrium away from coking, thereby lowering the critical current density and reducing the permanent degradation[3].

While 7 cells were processed and tested, current interruptions were only successfully run on two of the cells. The other samples were not usable due to four issues: 1) Many of the cells experienced rapid degradation, which may have been the result of using a new ceramic sealant that contained silicates. When silver was used as a sealant, the degradation was decreased. 2) Several of the cells started at extremely low power and demonstrated non-standard cathode polarization improvements upon initial testing. However, the problem was mitigated by using new LSM-YSZ inks for the cathode material. 3) It was noted during processing that the PSZ barrier layer did not make flat contact with the anode (due to the curvature of the cell). It seemed that the gas pocket should have no effect; however, the consequences were not investigated. 4) Many of the cells did not stabilize on methane - the voltage would drop to zero, regardless of the current run. Gas Chromatography (GC) data showed that the gaseous flow out of the cell was predominantly methane, with very little hydrogen gas or reaction byproducts, which indicated a lack of internal reforming. However, a potential solution was utilized for the final sample tested: by ramping the anode up to 800°C in an oxidizing environment, *i.e. air*, organic impurities in the silver seal would burn off. Subsequent reduction of NiO to Ni in the anode was then completed to prepare the SOFC for electrical operation. This technique was found to be quite successful for testing and should be used as standard operating procedure for future testing.

While the aforementioned problems did slow progress throughout the project, the final two samples did successfully yield current interruption data. These cells will be denoted as samples A and B. Though the

cells came from the same processing batch, there were some notable differences in their preparation and performances. Sample A was not able to stabilize on methane as mentioned above, and therefore only hydrogen current interruptions were carried out. The anode of sample B was oxidized at 800°C as mentioned previously, and therefore the cell was successfully operated on 70 sccm humidified methane. The expected power density of the cells in 50 sccm humidified H_2 (with PSZ barrier layers) was 675 mW/cm^2 at 750°C[1]. Sample A reached approximately 630 mW/cm^2, while sample B was approximately 500 mW/cm^2. The cause of the low power density for sample B was unknown; however, the OCV was also low (1.020 V), so it is likely that imperfect sealing allowed oxygen into the anode. The plots below summarize the current interruptions, both in humidified H2 and humidified CH4 (see the Appendix for additional figures).

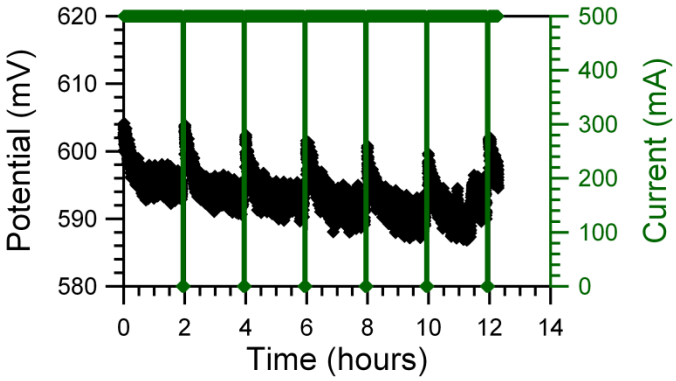

Figure 1: Sample A: 5 minute interruptions (with 115 min recovery time) on humidified hydrogen

Figure 1 demonstrates the effects of current interruptions on hydrogen for sample A. In each of the current interruption data sets, it appears that degradation is occurring. It is important to note, however, that all cells demonstrated baseline degradation during constant operation. To correct for this, the degradation rate was checked against the baseline degradation for each set of current interruptions. In the case of the hydrogen current interruption sets (2 minutes and 5 minutes), it was not clear that either featured degradation significantly above the baseline. The impedance and IV data gathered before and after current interruptions agreed: there was no change in ohmic loss, cell polarization, or power density. This matches expectations from literature.

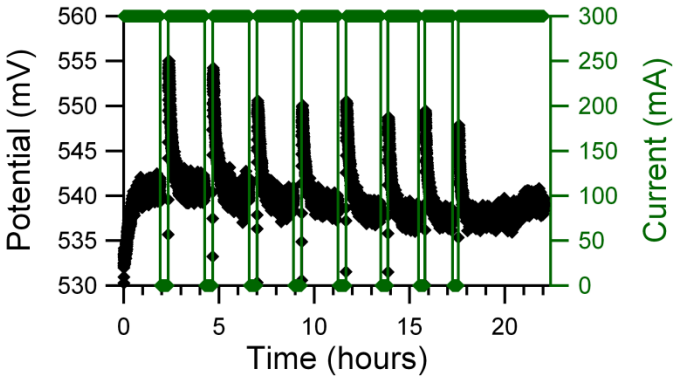

Figure 2: Sample B: 25 minute interruptions (with 115 min recovery time) on humidified methane

Current interruptions on methane for sample B demonstrated no degradation above baseline degradation at several time lengths of interruptions: 2, 5, 10, 15, and 25 minutes. For instance, the 25 minute interruptions shown in Figure 2 degraded by about 0.2 mV/hr, which matches the baseline rate.

However, there were inconsistencies within the data: for instance, the 15 minute interruptions showed degradation well above the baseline and the other interruption sets. However, the tentative conclusion is that no permanent degradation from coking occurred on methane current interruption sets of 25 minutes or less.

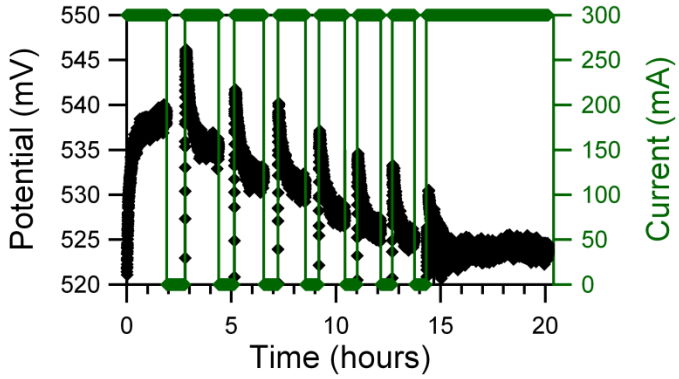

Figure 3: Sample B: 60 minute interruptions (with 120 min recovery time) on humidified methane

Permanent degradation is evident in Figure 3, which shows 60 minute interruptions for sample B operating on methane. The interruptions yielded degradation of about 1 mV/hr, which is significantly above the baseline rate of 0.2 mV/hr. While it is expected that permanent degradation would occur with longer interruptions, the critical interruption time is expected to be on the order of 6 minutes, rather than 60 minutes[3]. This discrepancy may have been caused by a slight leak resulting in oxygen entering the anode, as previously mentioned. Additional oxygen would shift the thermodynamics away from coking, and therefore likely preserve the cell for a longer period of time. The presence of oxygen is backed by the fact that the OCV was low even when running on hydrogen. The conclusion reached is that permanent degradation of about 2 mV per interruption did occur in the 60 minute set.

There are several next steps and lessons that should be considered for future work. Firstly, burning off impurities at 800°C before reducing the cell should become standard procedure. Secondly, new cells should be flat, such that no gas pocket exists between the PSZ barrier layer and the anode. Thirdly, it would be ideal if future cells demonstrated no baseline degradation. Stable operation would isolate degradation due to coking and therefore increase confidence in the results. Lastly, operating at higher temperature and/or with shorter recovery times would emphasize the effects of coking and therefore improve quantitative analysis. Future work will benefit from the experience gained during the current project. In conclusion, the cells processed only demonstrated permanent degradation with current interruptions of 60 minutes or longer when operating on methane.

References

1. Lin, Y. B.; Zhan, Z. L.; Barnett, S. A., Improving the stability of direct-methane solid oxide fuel cells using anode barrier layers. *J. Power Sources* **2006,** *158* (2), 1313-1316.

2. Wilson, J. R.; Gameiro, M.; Mischaikow, K.; Kalies, W.; Voorhees, P. W.; Barnett, S. A., Three-Dimensional Analysis of Solid Oxide Fuel Cell Ni-YSZ Anode Interconnectivity. *Microsc. microanal.* **2009,** *15* (1), 71-77.

3. Pillai, M. R.; Jiang, Y.; Mansourian, N.; Kim, I.; Bierschenk, D. M.; Zhu, H. Y.; Kee, R. J.; Barnett, S. A., Solid oxide fuel cell with oxide anode-side support. *Electrochem. Solid State Lett.* **2008,** *11* (10), B174-B177.

Appendix

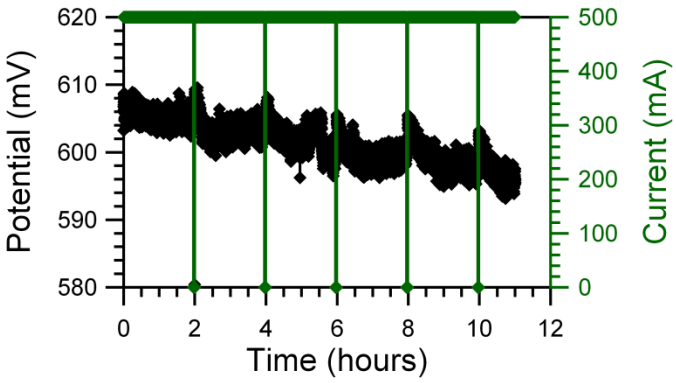

Figure 4: Sample A: 2 minute interruptions (with 118 min recovery time) on humidified hydrogen

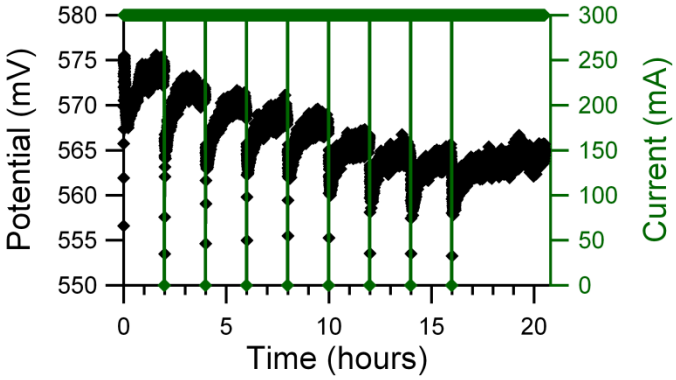

Figure 5: Sample B: 2 minute interruptions (with 118 min recovery time) on humidified methane

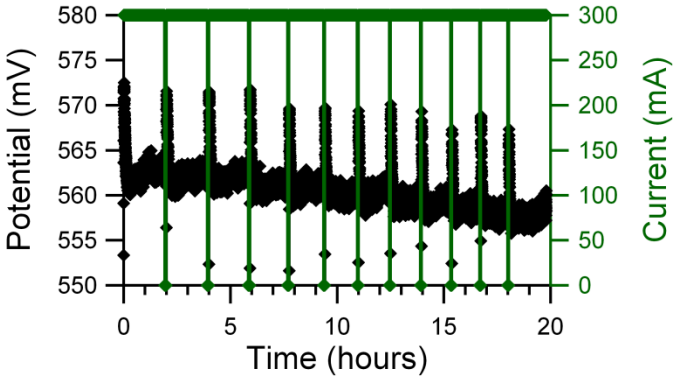

Figure 6: Sample B: 5 minute interruptions (with 115 min recovery time) on humidified methane

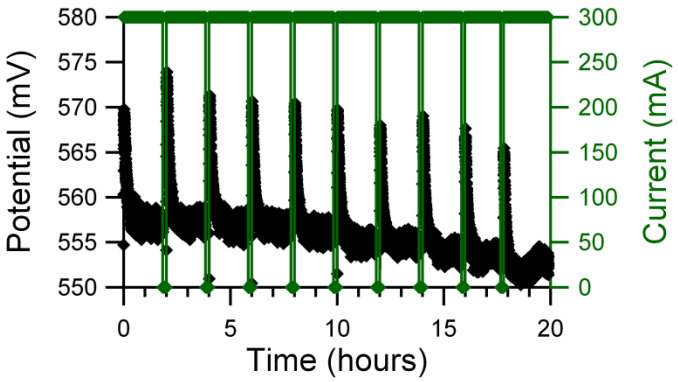

Figure 7: Sample B: 10 minute interruptions (with 110 min recovery time) on humidified methane

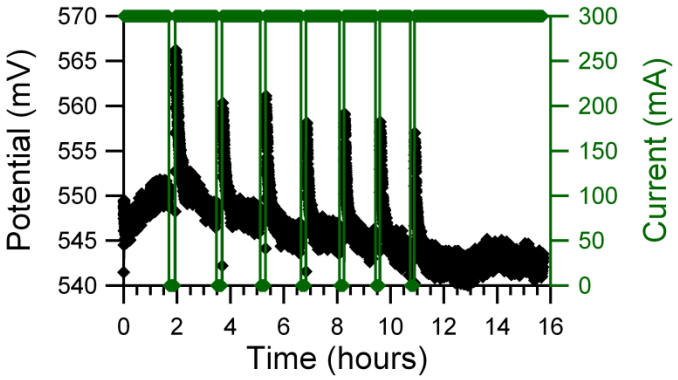

Figure 8: Sample B: 15 minute interruptions (with 105 min recovery time) on humidified methane