Performance and Durability of Solid Oxide Electrolysis Cells for Syngas Production

X. Sun, M. Chen, P. Hjalmarsson, S. D. Ebbesen
S. H. Jensen, M. Mogensen, P. V. Hendriksen

Fuel Cells and Solid State Chemistry Division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark, DK-4000 Roskilde, Denmark

Performance and durability of Ni/YSZ based solid oxide electrolysis cells (SOECs) for co-electrolysis of H2O and CO2 at high current density were investigated. The cells consist of a Ni/YSZ support, a Ni/YSZ fuel electrode, a YSZ electrolyte, and a LSM-YSZ oxygen electrode. The cell durability was examined at 800°C and electrolysis current density of -1 or -1.5 A/cm² with 60% reactant (H2O+CO2) utilization. The cell voltage degradation showed a strong dependence on the electrolysis current density, with an overall cell voltage degradation rate of 0.24 mV/h at -1 A/cm² and of 0.82 mV/h at -1.5 A/cm². Electrochemical characterization of the cells showed that the degradation was mainly related to the LSM/YSZ electrode when operated at -1 A/cm², whereas at increased current density (-1.5 A/cm²), both the Ni/YSZ and LSM/YSZ electrodes showed degradation.

Introduction

In recent years, there has been an increased focus on development of solid oxide electrolysis cells (SOECs) for hydrogen or syngas (mixture of H₂ and CO) production as the SOECs offer a promising technology for efficient energy conversion. Via high temperature electrolysis in the SOECs, electrical energy can be converted into and stored as chemical energy such as H₂ and/or CO via electrolysis of H₂O and/or CO₂ [1-5]. From the energy conversion and storage point of view, co-electrolysis of H₂O + CO₂ is more attractive as compared to steam electrolysis, as the produced syngas can be further catalyzed into various types of synthetic fuels such as ethanol, dimethyl ether (DME) or synthetic diesel. These synthetic fuels possess higher volumetric energy density as compared to hydrogen and can be easily stored, transported and consumed based on current infrastructure [2-6]. For SOEC to become a competitive technology for commercialization, durability is one of the critical issues. Long-term stability for 5-10 years operation is generally required [6-7]. Moreover, it is advantageous to operate SOECs at high current density in order to decrease production cost, to make use of excess electricity produced from renewable energy such as wind or solar energy and to achieve high syngas production rate. In recent years, various efforts have been carried out to investigate degradation of SOECs under steam electrolysis [9-12], CO₂ electrolysis [13] or co-electrolysis [14-15] and different degradation mechanisms have been proposed. The suggested degradation mechanisms include segregation of impurity phases (from the raw materials) to the triple phase boundary (TPB) [11], poisoning of the electrodes by impurities from the gas stream [15], oxygen electrode delamination due to large oxygen activity gradients [9, 12, 16-17]. It has been reported that for SOECs operated at low...
electrolysis current density (below 1 A/cm²), impurities are the main cause for degradation. By cleaning inlet gas to the Ni/YSZ electrode, almost zero degradation has been demonstrated [15]. However, only very few reports [14] of SOEC durability under co-electrolysis at high current density are available in literature. The purpose of this work is to investigate performance and durability of SOECs under co-electrolysis of H₂O + CO₂ at electrolysis current densities above 1 A/cm².

Experimental

Planar Ni/YSZ-supported solid oxide cells were used in this study. The cells consist of a negative electrode with a thick Ni/YSZ porous support layer (~ 300 µm in thickness) and a Ni/YSZ active layer (10 µm in thickness), a ~12 µm thick 8 mol% Y₂O₃ stabilized ZrO₂ (YSZ) electrolyte and an LSM ((La₀.₇₅Sr₀.₂₅)₀.₉₅MnO₃)/YSZ composite oxygen electrode. The total cell area is 5 cm * 5 cm with an active electrode area of 4 cm * 4 cm (16 cm²). For testing the cells, a test house as described in details elsewhere [15] was used. The cell was for testing sandwiched between gas distribution layers (corrugated Au and Ni meshes on the oxygen electrode side and the hydrogen electrode side, respectively), current collectors (Au and Ni foils on the oxygen electrode side and the hydrogen electrode side, respectively), and alumina cell tell houses. The cell was sealed at its edges by glass. At start up, the cell was heated up to 850°C and Ni/YSZ electrode is reduced to Ni in H₂ + 4% H₂O.

In this work, three identical cells were tested labeled Cell-0, Cell-1 and Cell-2. Cell-0 was a reference cell where only reduction and initial performance characterization was performed. The initial performance were carried out by measuring DC polarization (i-V) curves and AC electrochemical impedance spectra (EIS) at 850, 800 and 750°C. Gas shift characterizations were performed in H₂/H₂O mixture by varying gas atmospheres at the Ni/YSZ electrode (by changing H₂O concentration) and the LSM/YSZ (Air or O₂) electrode respectively. The impedance spectra were measured under zero current using a Solartron 1255 frequency analyzer with an external shunt. The spectra were recorded from 82451 to 0.08 Hz with six points per decade. After the initial performance characterization, Cell-1 and Cell-2 were exposed to durability test under constant galvanostatic electrolysis conditions. Both tests were operated at 800°C with 10% H₂ + 45% H₂O + 45% CO₂ supplied to the Ni/YSZ electrode and oxygen to the LSM electrode. For Cell-1, the applied current density was -1 A/cm² and was tested for electrolysis durability for 932 hours. For Cell-2, the durability test started with -1 A/cm² for 60 hours and afterwards the current was increased to -1.5 A/cm² for 325 hours. A theoretical reactant (CO₂+H₂O) conversion was 60% for both tests (Cell-1 and Cell-2). In this study, the gases supplied to the Ni/YSZ electrode were cleaned before being fed into the cell, following the procedure described by Ebbesen et al. [18].

Results and discussion

Initial Performance Characterization

Figure 1 shows the i-V curves of Cell-0 recorded during initial performance characterization. For these measurements pure oxygen was supplied to the LSM/YSZ
electrode. The measured i-V curves are linear at low current density. No discontinuity occurred in the shift from fuel cell mode to electrolysis cell mode. In 10% H₂ + 45% H₂O + 45% CO₂, due to low H₂ content in the fuel gas, concentration polarization became significant at current density above 0.25 A/cm² in fuel cell mode.

**Figure 1. Initial performance of solid oxide cell.**

EIS were recorded during the initial performance characterizations. The area specific resistance (ASR) for Cell-0 derived from EIS for 50% H₂ + 50% H₂O is 0.404, 0.251 and 0.156 Ω·cm² at 750, 800 and 850°C respectively. The ASR values for 10% H₂ + 45% H₂O + 45% CO₂ are 0.486, 0.33 and 0.243 Ω·cm² at 750, 800 and 850°C, respectively. Similar initial performance was obtained for Cell-1 and Cell-2. Table 1 lists serial resistance (Rs), polarization resistance (Rp), and total cell area specific resistance (ASR) derived from EIS measurements at 800 and 850°C with 50% H₂ + 50% H₂O supplied to Ni/YSZ electrode and O₂ supplied to LSM/YSZ electrode. The three cells showed almost identical performance and only minor difference was observed (differences are most likely caused by small variations when mounting the cell in the test setup).

**Table 1 Initial Rs, Rp and ASR of the tested cells at 850 ºC and 800 ºC with 50% H₂ + 50% H₂O supplied to Ni/YSZ electrode and O₂ supplied to LSM/YSZ electrode.**

<table>
<thead>
<tr>
<th>Cell</th>
<th>850°C</th>
<th>800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rs /Ω·cm²</td>
<td>Rp /Ω·cm²</td>
</tr>
<tr>
<td>Cell-0</td>
<td>0.088</td>
<td>0.069</td>
</tr>
<tr>
<td>Cell-1</td>
<td>0.086</td>
<td>0.074</td>
</tr>
<tr>
<td>Cell-2</td>
<td>0.079</td>
<td>0.074</td>
</tr>
</tbody>
</table>
**Durability**

Figure 2 shows the cell voltages evolution with time for Cell-1 and Cell-2. The cell voltage data were obtained directly from the cell voltage measured during the durability test. The voltage fluctuation within the first 200 hours was caused by uneven steam supply. This problem was solved for the remaining tests. During the first 60 hours at electrolysis current density of -1 A/cm², Cell-1 and Cell-2 showed similar degradation rate, 0.60 and 0.64 mV/h for Cell-1 and Cell-2 respectively. For Cell-1, the current density was kept at -1 A/cm² for a total period of 920 hours, the cell degraded with a degradation rate of 0.422 mV/h for the first 200 hours, which decreased to 0.216 mV/h for the remaining period. For Cell-2, the current density was increased to -1.5 A/cm² after the initial period at -1 A/cm² (60 hours). At -1.5 A/cm², Cell-2 degraded with a degradation rate of 0.633 mV/h for the first 200h and then increased to 1.3 mV/h for the remaining period. The degradation rates observed in the present work are much higher than those reported for tests performed at lower current densities at Risø DTU [15]. It is clear that the degradation rate is significantly higher at electrolysis current density above 1 A/cm².

To examine cause of the degradation, EIS was recorded under current also during the electrolysis durability tests. From EIS measurements, the cell ohmic resistance (Rs) and electrode polarization resistance (Rp) can be deduced and the results are presented in Figure 3. For Cell-1, Rs increased with a rate of 0.06 mΩ·cm²/h for the first 400 h and afterwards with 0.15 mΩ·cm²/h for the remaining test period. For Cell-2, Rs increased with a rate of 0.027 mΩ·cm²/h for the first 200h and 0.46 mΩ·cm²/h for the remaining period. The Rs degradation rate is clearly dependent on the electrolysis current density. The Rp degradation did however not show a strong dependence on the current density. For Cell-1, Rp increased with a rate of 1.17 mΩ·cm²/h for the first 70 hours, whereas it slightly decreased (activation) for the next 100 hours and afterwards increased again but with a rate of 0.028 mΩ·cm²/h for the remaining period. For Cell-2, Rp increased with a rate of 0.098 mΩ·cm²/h for the first 70 hours and decreased slightly (activation) with a
rate of \(-0.023 \text{ m\Omega\cdotcm}^2/\text{h}\) for the remaining period. Unlike \(R_s\), the \(R_p\) degradation did not exhibit strong dependence on the electrolysis current density. From Figure 3, it can also be concluded that at current density above -1 A/cm\(^2\), the initial cell degradation is mainly due to \(R_p\) increase while the long term degradation is more related to \(R_s\) increase.

![Figure 3](image-url)

**Figure 3.** Cell resistance degradation with time for Cell-1 and Cell-2. (a) ohmic resistance degradation, (b) electrode polarization resistance degradation.

**ADIS Analysis of Cell Degradation during Electrolysis**

![Figure 4](image-url)

**Figure 4.** ADIS plot for Cell-1 during co-electrolysis at 800°C and -1 A/cm\(^2\).

To clarify possible degradation mechanisms, analysis of the difference in impedance spectra (ADIS) was performed[15]. The difference in impedance was calculated from the real part of the measured impedance \((Z'(f))\), according to Eq.1 with \(Z'(f)_{t=\text{reference time}}\) used as the reference. The first impedance spectra recorded after starting of electrolysis was used as the reference for ADIS analysis. The ADIS analysis method has been described in elsewhere [15]
\[
\frac{\Delta \delta Z'(f)}{\delta \ln(f)} = \frac{(Z'(f_{n+1}) - Z'(f_{n-1}))_{i_t} - (Z'(f_{n+1}) - Z'(f_{n-1}))_{t_{\text{reference time}}}}{\ln(f_{n+1}) - \ln(f_{n-1})}
\]  

Figure 4 shows the ADIS plot of Cell-1 during co-electrolysis of 10% H\textsubscript{2} + 45% H\textsubscript{2}O + 45% CO\textsubscript{2} at 800°C and -1 A/cm\textsuperscript{2}. Two major changes in \( \Delta \delta Z'(f)/\delta \ln(f) \) can be seen from Figure 4, one at frequency above 10 kHz with a summit frequency of 26 kHz and the other at frequency around 100-1000Hz. A resistance increase and a frequency shift were involved in both cases. According to the previously reported characteristic frequencies for similar cells produced at Risø DTU [19], both the high frequency range above 10 kHz and the middle frequency range (100 Hz – 1 kHz) may be related to electrochemical processes taking place at the LSM/YSZ electrode.

![Figure 4. ADIS plot of Cell-1 during co-electrolysis of 10% H\textsubscript{2} + 45% H\textsubscript{2}O + 45% CO\textsubscript{2} at 800°C and -1 A/cm\textsuperscript{2}.](image)

Figure 5. ADIS plot for Cell-2 during co-electrolysis at 800°C and -1.5A/cm\textsuperscript{2}. Reference time used for ADIS analysis is when applying -1.5A/cm\textsuperscript{2} after 60h operation at -1A/cm\textsuperscript{2}.

The ADIS plot for Cell-2 tested at -1.5A/cm\textsuperscript{2} is given in Figure 5. Three major degradation processes were observed. The degradation processes with a characteristic frequency of above 20 kHz and around 1 kHz may be assigned to possible degradation at the LSM/YSZ electrode. The low frequency range below 100 Hz may be related to gas diffusion and gas conversion mainly at the Ni/YSZ electrode as reported previously [19].

**Gas Shift Analysis by EIS**

In order to break down impedance contributions from each of the two electrodes, gas shift impedance spectra were measured before and after electrolysis tests, by changing the composition of supplied gases to either Ni/YSZ or LSM electrode. Gas shift ADIS analyses were then carried out based on the measured impedance spectra. For gas shift analysis at the Ni/YSZ electrode, impedance spectra were recorded at zero current, the shift of gas composition was from 50% H\textsubscript{2} + 50% H\textsubscript{2}O to 80% H\textsubscript{2} + 20% H\textsubscript{2}O while keeping O\textsubscript{2} to the LSM electrode. For gas shift analysis at the LSM electrode, the shift of gas composition was from O\textsubscript{2} to air while keeping 50% H\textsubscript{2}+50% H\textsubscript{2}O at the Ni/YSZ electrode.
The difference in impedance is calculated according to Eq. 2-3. Where $f_{n+1}$ is the n+1 measurement frequency and $Z'(f_{n+1})$ is the real part of $Z$ at the n+1 measurement frequency.

$$
\frac{\partial Z'(f_{\text{Ni/YSZ}})}{\partial \ln(f)} = \frac{(Z'(f_{n+1}) - Z'(f_{n-1}))_{80\%H_2-20\%H_2O} - (Z'(f_{n+1}) - Z'(f_{n-1}))_{50\%H_2-50\%H_2O}}{\ln(f_{n+1}) - \ln(f_{n-1})} \tag{2}
$$

$$
\frac{\partial Z'(f)_{\text{LSM}}}{\partial \ln(f)} = \frac{(Z'(f_{n+1}) - Z'(f_{n-1}))_{\text{air}} - (Z'(f_{n+1}) - Z'(f_{n-1}))_{\text{O}_x}}{\ln(f_{n+1}) - \ln(f_{n-1})} \tag{3}
$$

The gas shift impedance plots of Ni/YSZ electrode and LSM/YSZ electrode for Cell-1 are shown in Figure 6. When changing gas composition at Ni/YSZ electrode, a small increase in $\partial Z'(f)/\partial \ln(f)$ with a summit frequency shifting from 2 kHz to around 900 Hz was observed (Figure 6a). For the LSM/YSZ electrode, a relatively big increase in $\partial Z'(f)/\partial \ln(f)$ with the summit frequency shifting from around 1 kHz to 250 Hz was observed. This indicates that the degradation for Cell-1 is to a large extent related to the LSM/YSZ electrode. This is in good agreement with the ADIS analysis during electrolysis as shown in Figure 4.

![Figure 6. Gas shift ADIS analysis of Cell-1 before and after electrolysis. (a) ADIS for Ni electrode, (b) ADIS for LSM electrode;](image)

The gas shift impedance plots of the Ni/YSZ electrode and the LSM/YSZ electrode for Cell-2 are shown in Figure 7. Significant changes in $\partial Z'(f)/\partial \ln(f)$ can be seen on both electrodes. At the Ni/YSZ electrode, a significant increase in $\partial Z'(f)/\partial \ln(f)$ was observed with a shift of summit frequency from several kHz to 400 Hz (Figure 7a). At the LSM/YSZ electrode, a big increase in $\partial Z'(f)/\partial \ln(f)$ was found at the summit frequency around 850 Hz (Figure 7b). It can therefore be concluded the degradation in Cell-2 is related to both the Ni/YSZ and the LSM/YSZ electrode, which is also in good agreement with the ADIS analysis during electrolysis as shown in Figure 5.
Conclusion

Performance and durability of solid oxide electrolysis cells (SOEC) for co-electrolysis of H$_2$O + CO$_2$ were studied at 800°C and electrolysis current density of -1 or -1.5 A/cm$^2$. The cell voltage degradation showed a strong dependence on the electrolysis current density, with an overall degradation rate of 0.24 mV/h at -1 A/cm$^2$ and of 0.82 mV/h at -1.5 A/cm$^2$. Results from impedance measurements during test indicate that the initial cell degradation was mainly due to an increase in polarization resistance while the long term degradation was to a large extend caused by an increase in the serial resistance indicating structural changes of the electrodes. Based on detailed impedance analyses before, during and after test, it was concluded that the cell degradation at -1 A/cm$^2$ was related to the LSM/YSZ electrode mainly. Operating the cell at -1.5 A/cm$^2$, both the Ni/YSZ and LSM/YSZ electrodes contributed to the overall cell degradation.

Acknowledgment

This work was financially supported by the Energinet.dk through the project ForskEL 2010-1-10432 “planSOEC-R&D and commercialization roadmap for SOEC electrolysis”. Topsoe Fuel Cell A/S is acknowledged for providing the cells.

References