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TASK 6 NON-PROPRIETARY STACK RESEARCH

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TITLE: NON-PROPRIETARY STACK RESEARCH

CONTRACT: DE-AC21-90MC27168

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OBJECTIVES: The objectives are to identify technical research issues and to develop understanding as well as quantification of carbonate fuel cell ohmic resistances.

PROGRESS BY SUBTASK

SUBTASK 6.1 Identify Technical Research Issues

The purpose of this subtask is to review outstanding carbonate stack issues and to identify those which are impeding the attainment of performance and/or life goals. Approach(es) for resolution of each of the critical issues will be defined. Research efforts, leading to resolution of each of specific issues will be defined and proposed to COR. There is no activity on this subtask this quarter.

SUBTASK 6.2 Conduct Non-proprietary Research

OBJECTIVES

The overall objective of the current Subtask 6.2 is to develop understanding as well as quantification of cell ohmic resistance in carbonate fuel cell. The important resistance-contributing interfaces and elements are being investigated in high-temperature out-of-cell resistance experiments, using an AC-impedance technique. It is expected that this research effort will provide insight to establish design providing low cell resistance and stable performance.

GENERAL BACKGROUND

Ohmic resistance loss in a state-of-the-art carbonate fuel cell contributes about 65 mV loss at BOL (beginning-of-life). It may increase to about as much as 145 mV after 40,000 hours. Its reduction will offer further improvement in fuel cell power plant efficiency. The important resistance contributing elements/interfaces are illustrated in Figure 1. The majority of the ohmic loss is attributed to electrolyte matrix (ionic) and cathode-side hardware (electronic)[1,2]. The ohmic loss due to electrodes and anode-side hardware can generally be neglected.

The matrix ionic resistance is influenced by many factors: electrolyte conductivity, matrix porosity, tortuosity,

FIGURE 1: IMPORTANT RESISTANCE CONTRIBUTING INTERFACED ELEMENTS:

THE MAJORITY OF THE RESISTANCE IS CONTRIBUTED BY MATRIX AND CATHODE-SIDE CONTACT

electrolyte fill level and matrix thickness. At present, matrix contributes to $> 300 \text{ m}\Omega\text{cm}^2$ ($>70\%$ of the total cell ohmic resistance) and is the major resistance contributor.

The oxide formed at the cathode-CCC(cathode current collector) interface is the major cause of the cathode-side hardware resistance (contributing about $60 \text{ m}\Omega\text{cm}^2$). The oxide in general has a bi-layered structure (LiFeO_2 outer and Cr-rich inner scales). Altering this oxide structure and composition has the potential of improving this resistance.

Another potential ohmic-loss area is the CCC-BP(bipolar plate) interface. This contact interface generally contributes to very low ohmic loss ($< 10 \text{ m}\Omega\text{cm}^2$)[1] for several thousand hours if the contact area remains adequate. However, oxide scale can eventually form at this interface and contributes to a higher resistance for longer-term operation.

For carbonate fuel cell to be economically viable, a 40,000h life is needed. Therefore, resistance stability for such a long-term operation is very important. Increase of the matrix resistance is mainly caused by electrolyte loss to hardware surface. Increase of the cathode-CCC resistance is mainly due to continuous thickening of the corrosion oxide scale. Increase of the CCC-BP resistance can be caused by the loss of contact and subsequent oxide formation there. However, the relative contribution of the above resistance increases is not yet clear.

Based on the above discussion, more understanding on ohmic resistance, particularly its increase, is needed for better recommending approaches to further reduce the ohmic resistance. The present task is a follow-up on earlier resistance study[1,2] and focuses on the effect of many variables on the resistance of various interfaces/elements.

EXPERIMENTAL

Ohmic resistance experiments to evaluate resistance of each interfaces/elements are being conducted in carbonate fuel cell environment. The test rig illustrated in Figure 2 is used. The resistance is measured using an AC-impedance technique. The experimental variables include current collector geometry(providing different contact areas), grain size and composition(310S and 316L), surface oxide(formed during annealing), electrolyte composition(Li/K, Li/Na, etc.), compressive force and aging time(1000-10,000 hours).

The post-test analysis include thorough washing of current collector and bipolar plate to determine electrolyte loss to the cathode-side internal hardware. The cathode is digested to determine electrolyte fill level and the extent of lithiation. The current collector and bipolar plate surfaces are examined for the contact pattern. Cross-sectional analysis is performed to determine oxide structure and thickness, particularly at the

FIGURE 2: OHMIC RESISTANCE EXPERIMENTAL FACILITY:
 HOT CORROSION OHMIC RESISTANCE EXPERIMENTS ARE PERFORMED SIMULTANEOUSLY

cathode-CCC contact interface, using SEM/EDS.

RESULTS

So far, about ten experiments have been performed. The results are summarized as follows:

Cathode-CCC Interface

Oxide formed at this interface contributes to about 50-60 mΩcm² BOL(100 hours) resistance (about 8-10 mV loss @ 160 mA/cm²) if the overall contact here is about 40%. A typical post-test oxide morphology is shown in Figure 3. The outer scale is basically LiFeO₂ doped with a large amount of Ni (>20 mole%, mainly from NiO cathode) and a small amount of Mn (<3 mole %, from stainless steel substrate). Its specific ohmic resistivity was reported to be 30 Ωcm or larger[3]. The Cr content here is very low (<2 mole%). The inner scale is very rich in Cr but also contains significant amount of Fe and Ni.

The overall scale specific resistivity, normalized for contact area and NiO porosity, is shown in Table 1. The oxide formed on 310S stainless steel is thinner but more resistive, likely due to its more compact inner chromia scale ($\rho=100$ Ωcm). The inner scale on 316L is thicker as well as higher in Fe content; therefore, it is less protective but likely more electronically conductive. This may explain the lower overall specific resistivity for the oxide formed on 316L. The oxide formed on large-grained 316L is slightly thicker but with a slightly lower specific resistivity. The overall oxide ohmic loss is therefore similar to that on fine-grained 316L.

Improvement in conductivity of both the inner and outer oxide layers (to < 1.0 Ωcm) by modifying oxide structure and composition, but without sacrificing overall corrosion resistance, is needed.

CCC-BP Interface

The CCC-BP interface generally contributes to only negligible ohmic loss (<10 mΩcm²), if the contact can be well maintained. However, if the contact is small (for the example shown in Figure 4, for an experimental current collector), the interfacial resistance was found to increase to >50 mΩcm² after 1000h testing. Post-test analysis revealed the formation of thick oxide at the contact area. To avoid high CCC-BP contact resistance, a contact of >20% is desirable. Moreover, oxide present at BOL may have an effect.

A thin chromia scale (<0.1 mils) can form on CCC surface during annealing. The ohmic resistance tests showed that this layer may cause a resistance increase of more than five times (Figure 5). Examination of the post-test contact showed the oxide formed at this contact during annealing was thick (Figure 6). To

(a) 316L
1400h Testing

(b) 310S
2150h Testing

X1K 10 μ m

FIGURE 3: POST-TEST OXIDE MORPHOLOGY:

Fe-RICH OUTER SCALE AND Cr-RICH INNER SCALE IS APPARENT IN BOTH 316L AND 310S MATERIALS

TABLE 1: OXIDE SPECIFIC OHMIC RESISTIVITY

MATERIAL	OHMIC RESISTIVITY (Ωcm)
310S	~ 40
316L FINE-MEDIUM GRAINED	15-25
316L LARGE-GRAINED	~ 15

BIPOLAR PLATE SURFACE

CONTACT AREA ENCIRCLED

FIGURE 4: EXAMPLE OF POOR CCC-BP CONTACT:

10 mV LOSS CAN BE ATTRIBUTED TO THIS CONTACT

FIGURE 5: EFFECT OF ANNEALING ON CCC-BP CONTACT:

TOO MUCH OXIDE FORMATION DURING ANNEALING CAN CAUSE HIGH OHMIC LOSS

FIGURE 6: POST-TEST CONTACT PATTERN:

POOR CCC-BP CONTACT (WITH THICK SCALE) IS APPARENT IN THE RIGHT PHOTOGRAPH

avoid this problem, bright lower-temperature annealing is desirable.

The oxide formed on CCC during annealing, however, does not cause an increase of the cathode-CCC contact resistance. This can be explained by the dissolution and disappearance of this chromia scale into carbonate (as chromate) during initial cell start-up.

Matrix Ionic Resistance

Matrix contributes to $>300 \text{ m}\Omega\text{cm}^2$ ohmic loss and has the highest potential for further resistance reduction. According to the Bruggman equation (an ideal case), the matrix resistivity is inversely proportional to the 1.5th power of the matrix porosity (i.e. $\rho \propto \epsilon^{-1.5}$). An actual carbonate fuel cell has a larger effect than predicted by the 1.5th power factor. Nevertheless, based on the Bruggman equation, an increase of matrix porosity by a mere 5% (e.g., 45% $\rightarrow$ 50%) can reduce the matrix resistance by 15%. A switch from Li/K to Li/Na has the potential of reducing matrix resistivity by additional 40%. Therefore, a matrix with low tortuosity, high porosity and conductive electrolyte has the highest potential of reducing cell resistance significantly.

Electrolyte loss to hardware surface is important for long-term stability of matrix resistance. The creepage electrolyte (washable by dilute acid) is generally rich in potassium and chromium. The loss appears to be higher with high Cr steel. It is possible that Cr can easily dissolve into molten carbonate as chromate and form low melting-point or more wettable melt mixture. This melt can in term travel easily on CCC surface. Also, electrolyte creepage loss is significantly higher on CCC of higher surface area (Figure 7). Therefore, CCC of low surface area and minimal Cr content required for protective scale formation is recommended.

The oxide scale was also completely digested to determine the amount of chemically attached Li and K (corrosion electrolyte loss). The lost electrolyte consists mainly of Li (>90%), due to the stable lithium ferrite scale formation. It is also interesting that the corrosion electrolyte loss is not as strongly affected by the CCC surface area as the creepage electrolyte loss. It is postulated that Li is mostly incorporated into the scale formed at or near the cathode-CCC interface while potassium (as potassium chromate-carbonate mixture and not chemically attached to the scale) continues to travel on the surface away from the cathode. Therefore, the Li loss to corrosion scale is not strongly affected by the CCC surface area.

Based on the electrolyte loss study so far, electrolyte loss to the internal hardware for cells with low surface area CCCs and with proper selection of material can be projected to be less than 25% of the BOL electrolyte inventory.

FIGURE 7: 40,000h PROJECTION OF ELECTROLYTE LOSS TO INTERNAL HARDWARE:

<25% BOL INVENTORY LOSS TO INTERNAL HARDWARE CAN BE PROJECTED

FUTURE WORK

The future work will include an investigation of the oxide scale (particularly the inner Cr-rich scale) formed at the cathode-CCC interface, the evaluation of the effects of alternate electrolyte composition (e.g., Li/Na) and the incorporation of corrosion products (Fe and Cr) into NiO cathode on cell ohmic resistance.

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