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To be presented at:

5th European SOFC Forum
July 1-5, 2002
Lucerne, Switzerland

* Work supported by the U.S. Department of Energy, Office of Advanced Automotive Technologies, Office of Transportation Technologies, under Contract W-31-109-ENG-38.

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ABSTRACT

Solid oxide fuel cells (SOFCs) are one of the potentially most efficient and clean energy conversion technologies for electric utility applications. Laboratory cells have shown extraordinary durability, and actual utility-scale prototypes have worked very well. The main obstacle to commercialization has been the relatively high manufacturing cost.

To reduce these costs, efforts have been underway for several years to adapt manufacturing technology from the semiconductor industry to the SOFCs; however, tape casting, screen printing and similar methods are more applicable to planar configurations than to the more proven tubular ones. In planar cells the bipolar plate and edge seals become more critical elements, and material selection may have repercussions for the other fuel cell components. Ferritic stainless steel bipolar plates may be a good choice for reducing the cost of the stacks, but ferritic steels oxidize rapidly at temperatures above 800°C. Inexorably, one is led to the conclusion that anodes, cathodes and electrolytes operating below 800°C need to be found.

Another motivation for developing planar SOFCs operating at reduced temperature is the prospect of new non-utility applications. The U.S. Department of Energy has initiated the Solid State Energy Conversion Alliance (SECA) program for developing small modular stacks ranging in capacity from 5 to 10 kW⁽¹⁾. This size range meets the power requirements of auxiliary power units for heavy and perhaps even light-duty vehicles, and also for remote stationary applications.

In terms of electric capacity, the distributed electric utility market may well exceed the potential market for APUs, but the number of units produced could be higher for the latter, yielding cost benefits related to mass production. On the other hand, the fuel for use in transportation or remote stationary applications will consist of gasoline, diesel or propane, which contain higher sulfur levels than natural gas. Anodes with some resistance to sulfur poisoning would be desirable. Also, during the more frequent shutdowns and startups in these applications, the anodes may get exposed to air. Typical nickel-based SOFC anodes may not tolerate air exposure very well and may need to be modified.

Argonne National Laboratory is engaged in developing new materials options for SECA applications, as discussed here.

ELECTROLYTES

Historically, the operating temperature of SOFCs was determined by the conductivity of the zirconia electrolyte. A conductivity of $10^{-1} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$ was needed for electrolyte-supported cells of about $200 \text{ }\mu\text{m}$ thickness. Yttrium-doped zirconia meets this requirement, as shown in Figure 1. By decreasing the thickness of the electrolyte to $10\text{--}20 \text{ }\mu\text{m}$, YSZ can be used at temperatures between 700 and 800°C , but such thin electrolytes will need to be mechanically supported. Scandium-doped zirconia and lanthanum gallate are more conductive and could be used at still lower temperatures. Gadolinium-doped ceria is another option, but it becomes a mixed conductor above about 600°C at anode condition and has a higher thermal expansion coefficient than zirconia. Different anode and cathode materials would therefore be needed for zirconia or ceria electrolytes.

In our work we explore both options; thin-film YSZ electrolytes with a target operating temperature between 700 and 800°C , as well as the low-temperature doped-ceria electrolytes for operation between 500 and 600°C . The lower the tolerable operating temperature, the less stringent the requirements on the metallic interconnect, allowing cheaper alloys to be used and, for certain applications, resulting in faster start-up times.

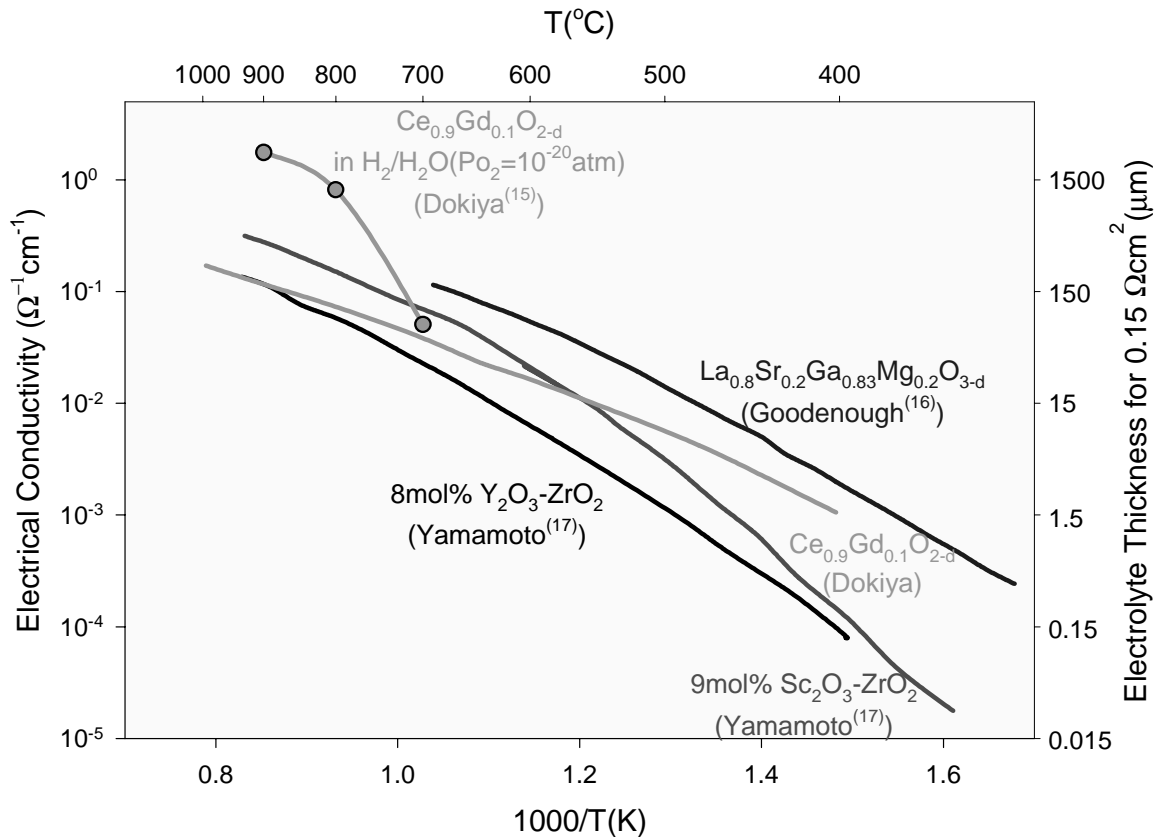


Figure 1. Comparison of Ionic Conductivities for Various Electrolytes.

CATHODES

Lanthanum manganite doped with 20% strontium has been the preferred cathode material in most SOFCs.⁽²⁾ It has reasonably good electronic conductivity but the oxide ion conductivity is marginal even at 1000°C. With decreasing temperature, the oxide ion conductivity declines further as shown in Figure 2, causing the overpotential of the cathode to become unacceptably high.⁽³⁻⁵⁾

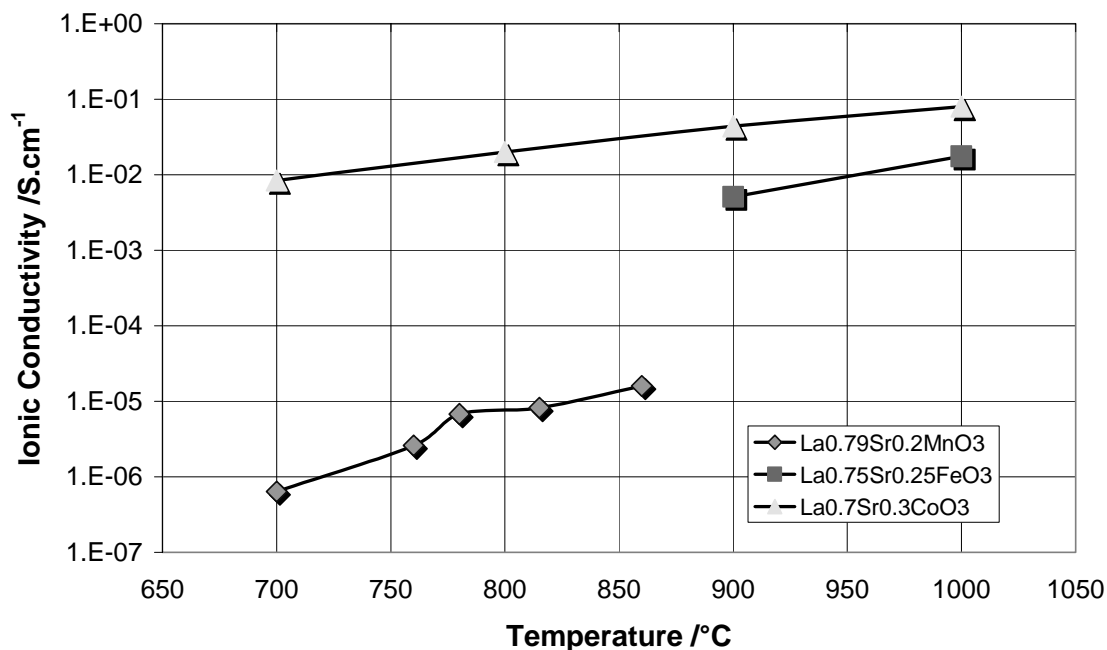


Fig. 2. Ionic Conductivities of Various Perovskite-Based Cathode Materials (Calculated from diffusion data).

Mixing lanthanum manganite with YSZ is one approach used by several fuel cell developers to overcome the oxygen transport limitation. At temperatures below 800°C such two-phase cathodes cannot support high current densities.

Ferrites, cobaltites and nickelites have better oxide ion conductivities than manganites but are also thermodynamically less stable. In contact with zirconia, lanthanum zirconate can form at the interface of the cathode and the electrolyte and yield high electrical resistances. Figure 3 shows area specific resistance of several lanthanum perovskites at temperatures ranging from 650 to 850°C. Lanthanum ferrite has the lowest interfacial resistance on zirconia electrolytes. The performance of the manganites is clearly inferior to the other classes of cathode materials, but with the exception of the ferrites, severe reactions were observed between the cathode and YSZ electrolyte, resulting in rapidly degrading long-term performance. Of the ferrites, strontium-doped lanthanum ferrite (LSF), achieved the lowest areal resistance and maintained a stable performance during long-term testing (500 hours). We believe that the improvement in performance is almost entirely due to the higher ionic conductivity in LSF compared with lanthanum strontium

manganite, which permits a larger surface area of the cathode to take part in the oxygen adsorption and reduction reactions. Further improvements are expected by optimizing the microstructure at the cathode-electrolyte interface.

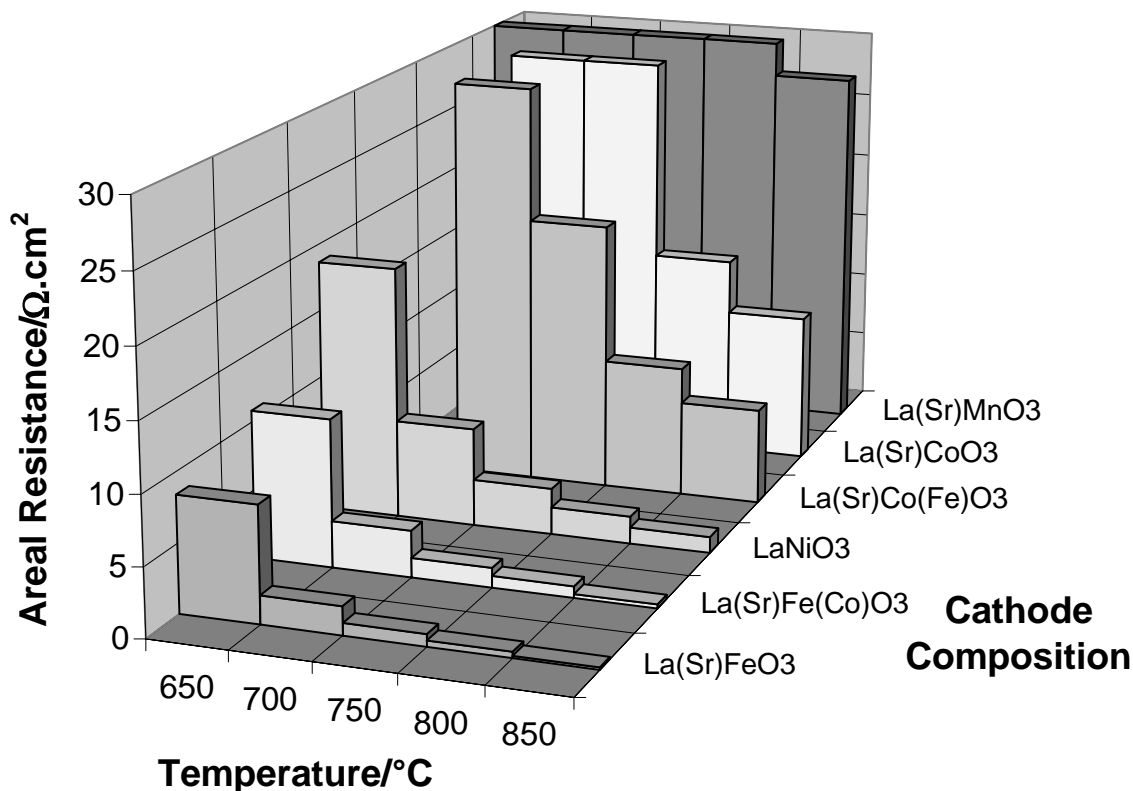


Fig. 3. Areal Resistances of Various Perovskite-Based Cathodes on YSZ Electrolytes.

Similar data for gadolinium doped ceria electrolytes in Figure 4 show that strontium-doped gadolinium cobaltite is an even better cathode material for CGO but not for YSZ, because of lanthanum zirconate formation on the latter.

The performance of LSF is not sufficient for use on CGO electrolytes because the electronic conductivity in this material is not adequate. Fortunately, the cobaltites do not react with CGO and thus we are able to take advantage of their better mixed conducting behavior compared with LSM and LSF, as cathode materials on CGO. The most widely used cathode on CGO is termed LSCF (a strontium and iron-doped lanthanum cobaltite). In this material a high strontium concentration is employed to further improve the conductivity of the material and a large addition of iron is doped on the B-site to better match the thermal expansion coefficient, which is generally too high in cobaltites, to that of YSZ. Our research has shown that changing the A-site cation to some of the alternative rare earths can further improve the performance of the cathode. Gadolinium proved to be the best option to date and by increasing the strontium concentration in this material to 50% yielded further improvement in performance. The explanation for the improvement in performance with the use of other rare-earth cations is not clear but in the case of Gd, which is also the dopant in the electrolyte, the elimination of one

potentially problematic cation is realized. The other rare earths do not fit into the ceria structure so well and may cause some elastic strain interference at the interface if they are able to diffuse into the electrolyte.

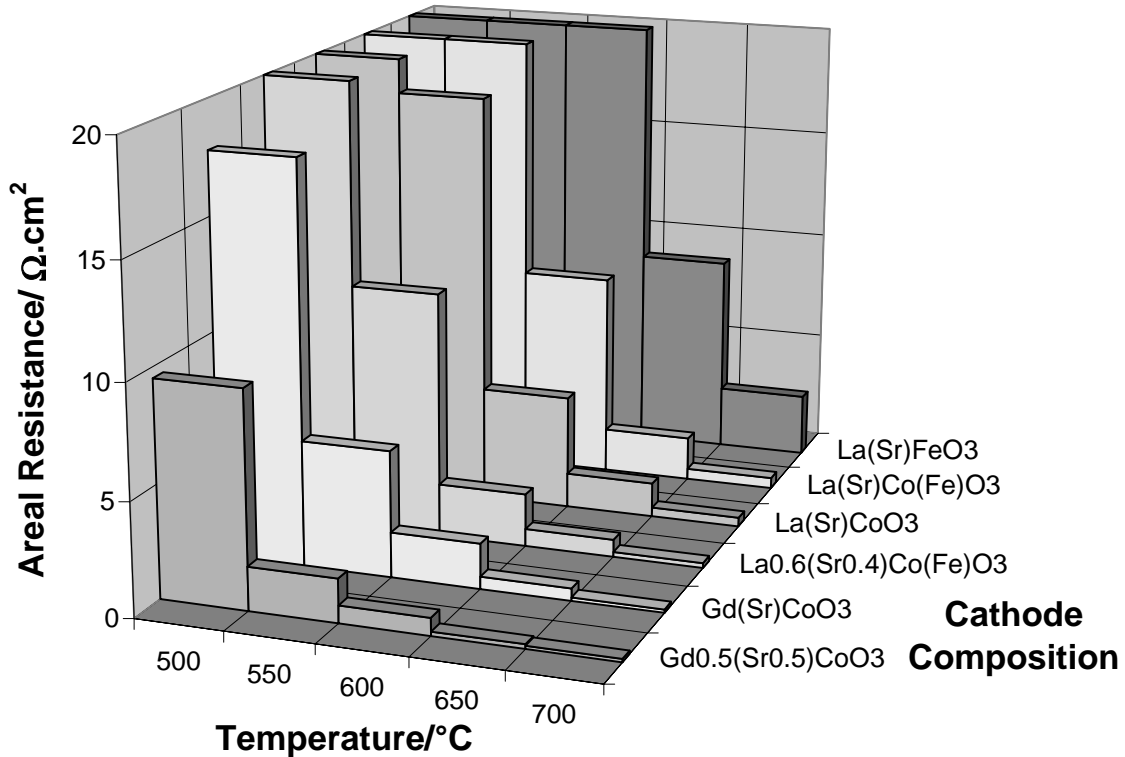


Fig. 4. Areal Resistance of Various Perovskite-Based Cathodes on CGO Electrolytes.

While the cathode resistance of this material is still not sufficiently low in the desired temperature range of 500-600°C, a significant reduction in resistance should be achievable by correct optimization of the microstructure.

Actual overpotential measurements as shown in Figure 5 confirm these results.⁽⁶⁻⁸⁾ The performance of LSF is clearly superior to that of LSM at 800°C. Figure 5 also shows the performance of a cobaltite on YSZ, the overpotential of which is higher than LSM. The performance of a similar cobaltite on a CGO electrolyte is substantially better, achieving cathodic overpotentials below 50 mV. This is a good demonstration of the negative affects that reaction with the YSZ electrolyte can have. Two LSF curves are shown in Figure 5. One is for measurements taken on day 1, while the second is taken nearly two weeks later with the cathode exposed to a constant current of 250 mA.cm⁻². Both curves show a big improvement over LSM at 800°C. The current conditioned LSF maintains an overpotential below 50 mV up to 300 mA.cm⁻² but increases above 50mV at higher current densities. With the improvements suggested in the discussion above we hope to further lower the overpotentials so that cathodic losses remain below 50 mV at higher current densities.

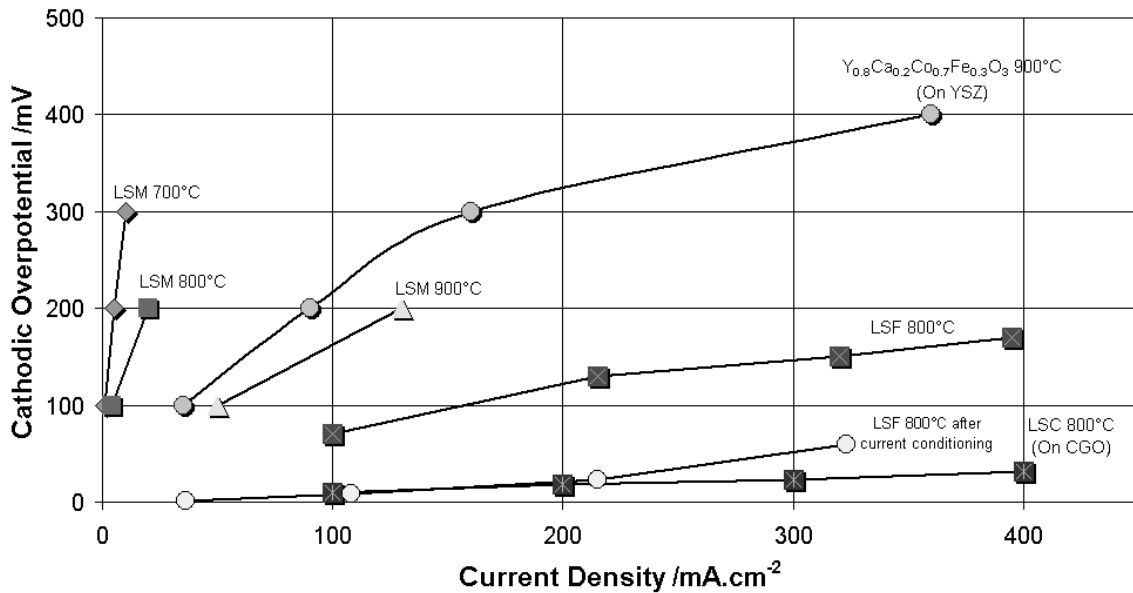


Fig. 5. Cathodic Overpotentials for Different Cathode Materials on CGO and YSZ.

ANODES

Nickel/zirconia cermets have been the standard anode material for many years. The sulfur tolerance is sometimes quoted as 1 ppm.⁽⁹⁾ Others have claimed higher numbers without disclosing compositional detail.

Titania-based perovskites⁽¹⁰⁾ are being explored for improved sulfur and oxygen tolerance but the performance is still marginal. There are very few other papers that discuss the problem of sulfur tolerance on the anode, and no real solution is currently available. A number of options are open to be explored, including the substitution or modification of the Ni site with other metals/alloys so that the sulfur does not poison the Ni sites. Other materials that would naturally be unaffected by sulfur can also be considered but their performance as an anode is, as yet, unknown.

BIPOLAR PLATES

In the tubular SOFC technology lanthanum chromite is used as the interconnect material. At 1000°C, it is chemically stable in fuel and air, has good electrical conductivity, and a thermal expansion coefficient that is closely matched to that of zirconia. However, it is difficult to sinter to full density, and in planar configuration it buckles due to oxide ion vacancies forming on the hydrogen side.

Ferritic stainless steels have thermal expansion coefficients similar to zirconia, and are oxidation-resistant up to temperatures of about 800°C. Various types of these ferritic steels have been used in planar SOFCs with good initial success⁽¹¹⁻¹³⁾. However, as the

oxide scale grows on these materials the electrical resistance increases. Over longer periods of time, it was found that the cathodic overpotential increased due to chromium contamination of the electrochemically active zone⁽¹⁴⁾. The chromium appears to have evaporated from the bipolar plate surface as a hydrous oxide.⁽¹⁸⁾ To overcome these limitations various coatings have been used in efforts to overcome these and improve performance. Chromium is critical for corrosion protection of the stainless steel in SOFCs because, unlike aluminum and silicon, it forms electrically conducting oxide layers. The challenge then is to inhibit evaporation.

Argonne has examined several commercially available ferritic stainless steels (430, 434, T-441, 444, 453, and E-Brite), received as sheets, with regard to their oxidation rates and the electrical resistance of the material after oxidation (up to 400 hours in humidified air). Most of these steels gave fairly similar results; those alloys with higher chromium content, and some silicon, typically fared better with respect to weight gain, which in turn gave lower resistances. Typical results gave resistances of $2.6\Omega\cdot\text{cm}^2$ and weight gains of 0.18 mg/cm^2 (after 400 hours). The T-441 and 453 were by far the worst performers. These alloys had approximately an order of magnitude larger weight gain and about a five-times increase in electrical resistance (attributed to a much thicker oxide scale). Based on these results, and the fact that 434 is the most available material, it was selected as a benchmark. Argonne is presently developing and testing a number of ferritic-based alloys both with and without chromium. The goals are to increase the electrical conductivity of the oxide scale, improve oxidation resistance, and prevent the problems associated with chromium migration within the fuel cell. Using the processing techniques developed at Argonne, we have compared these alloys to 434 (commercially available) processed using the same techniques. The results demonstrated that a number of the alloys developed at Argonne were superior to 434, and some were slightly superior to commercially available sheet materials with respect to electrical resistance after oxidation. Figures 6 and 7 compare one of the better Argonne alloys with 434 and 434 clad with this alloy.

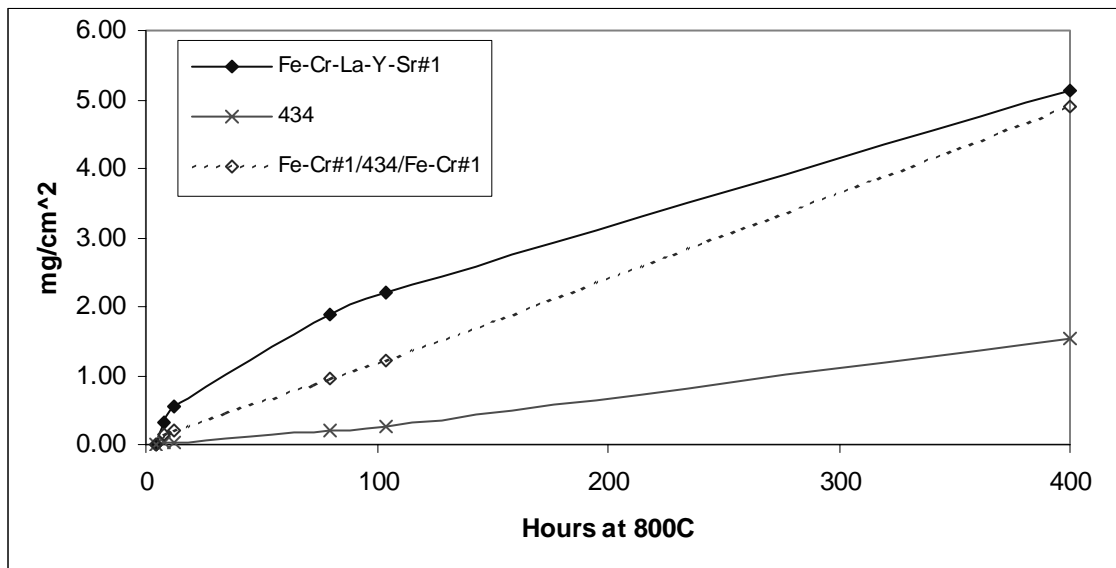


Fig. 6. Weight Gain of Corrosion Test Alloys Compared with 434 Stainless Steel.

It is easily seen that while the alloys show a larger increase in weight, the area specific resistance (ASR) of the Argonne alloy is much lower and the cladding provided similar properties to 434. Argonne continues to develop alloys and improve its processing techniques. Alloys produced without the traditional protective elements (aluminum, silicon and chromium) have also been tested. These alloys typically show much greater weight gains, but some have demonstrated ASR values around $5 \Omega\text{cm}^2$ even with large weight gains. It is hoped that with continued work on alloy design, the weight gain and electrical resistance can be further decreased.

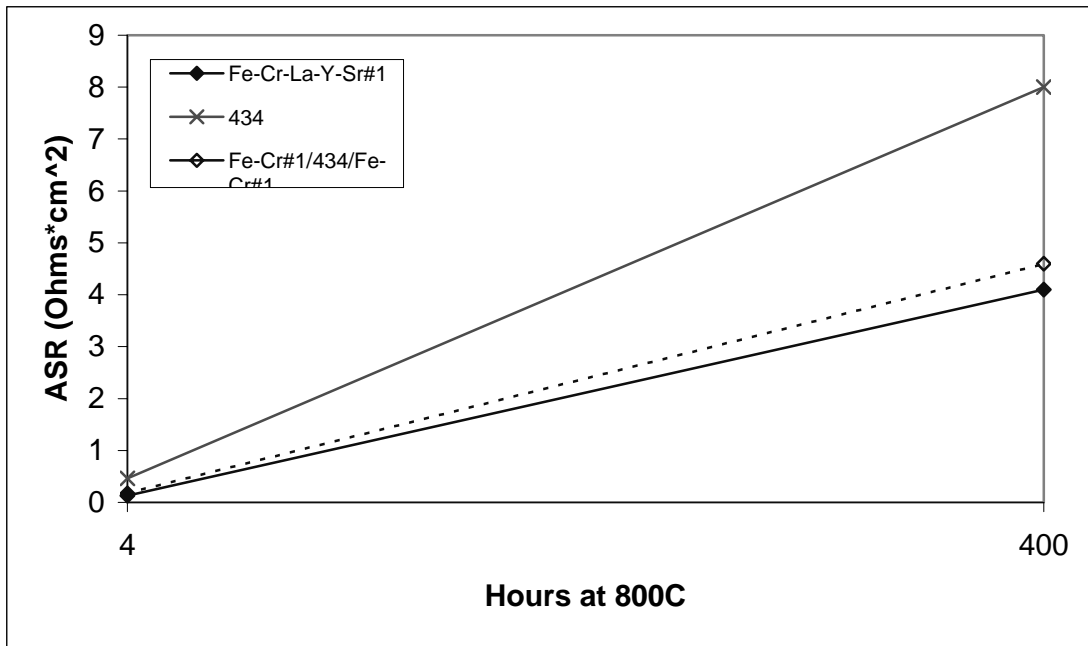


Fig. 7. Area Specific Resistance of Corrosion Test Alloys Compared with 434.

Developing alloys that form scales with the desired properties will offer advantages over coatings from several respects. The alloy would be self-healing should the scale be damaged, and no secondary processing step would be needed.

CONCLUSIONS

While there are still a number of materials issues yet to be fully resolved before the solid oxide fuel cell is ready for commercialization, Argonne has developed materials that show promise in solving several of the key issues. Ferrite-based cathodes, with further refinement, should be acceptable cathode materials on YSZ. Potential sulfur-tolerant anodes are under investigation and corrosion-resistant alloys that have low-scale resistances are already being prepared.

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