Materials Development for Improved Efficiency of Hydrogen Production by Steam Electrolysis and Thermochemical-Electrochemical Processes

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Introduction

We are investigating two processes as potential sources of hydrogen for the "hydrogen economy". One of these hydrogen production processes is water electrolysis at high temperatures using heat from a nuclear reactor, known as high temperature steam electrolysis (HTSE). The feasibility of this process is currently being demonstrated at Idaho National Laboratory using solid oxide fuel cell designs and materials[1]. A major source of efficiency loss in solid oxide electrolysis cells (SOECs) is poor electrode performance and durability resulting in large systems and high materials costs. The overall goal of our work in this area is to develop oxygen and steam electrodes for SOECs that will lead to improved performance and durability, and reduced costs.

Our approach to developing better-performing oxygen evolution electrodes for SOECs is to study materials with both high ionic and electronic conductivity at <1000°C, such as doped rare earth-transition metal perovskite oxides. We have also worked toward improving the performance of these perovskite electrodes by optimizing the microstructure and depositing a thin doped-ceria interlayer between the perovskite electrodes and zirconia electrolytes. The microstructure refinement involved functionally grading the electrode with small grains of the perovskite electrode material near the electrode-electrolyte interface to enhance the contact area, and large grains of the perovskite near the electrode-flow field interface to enhance the ability of product oxygen to diffuse through this region.

The other process under investigation is a hybrid thermochemical-electrochemical hydrogen production cycle that produces hydrogen from water, also using heat from a nuclear reactor. The proposed cycle is based on the sulfuric acid (H_2SO_4) synthesis and decomposition processes developed earlier (the "Westinghouse" process).[2]

$2\ H_2O + SO_2 \rightarrow H_2SO_4 + H_2$ – electricity	80°C	(1)
$H_2SO_4 \rightarrow H_2O + SO_3$	>450°C	(2)
$SO_3 \rightarrow SO_2 + 1/2\ O_2$	>800°C	(3)
$SO_3 \rightarrow SO_2 + 1/2\ O_2$ - electricity	500-600°C	(3-alternative)

The standard Westinghouse process requires temperatures over 800°C for step (3), the SO_3 decomposition reaction. In collaboration with the Japan Nuclear Cycle Institute (JNC), we are investigating means for lowering the temperature of the SO_3 decomposition to approximately 500°C to allow the use of a lower temperature heat source and to mitigate problems associated with corrosion at the higher temperatures.

The focus of our work at Argonne National Laboratory is the use of an oxide ion-conducting electrolysis cell to decompose SO_3 to SO_2. The goals of our work on this project are to: (1) perform thermodynamic analyses to confirm potential SO_2 yield as a function of temperature and cell conditions, (2) identify electrolyzer electrolyte materials with high oxide

ion conductivity at 500–600°C, and (3) determine the compatibility of candidate electrolyte materials with the highly reactive SO_3 atmospheres.

Experimental Procedures

Solid Oxide Electrolyzer Cell Electrode Preparation

Half cells of the oxygen electrode materials were fabricated for AC impedance spectroscopy. The half cells consisted of the test electrodes (0.38 to 0.6 cm² area) deposited on one side of a 200-μm thick YSZ (8 mol% yttria-stabilized zirconia) or SSZ (10 mol% scandia-1 mol% ceria-stabilized zirconia) plate and a platinum counter-electrode deposited on the opposite side. The cells also have reference electrodes, of the same composition as the test electrode, deposited on the same face of the electrolyte plate. The configuration of the test cell is shown in Figure 1. The platinum ink counter electrodes (Engelhard 6082) were applied to the substrates using the same masks used for the test electrodes (to ensure that the counter and working electrodes were of identical size) and fired at 850°C for 15 min in air.

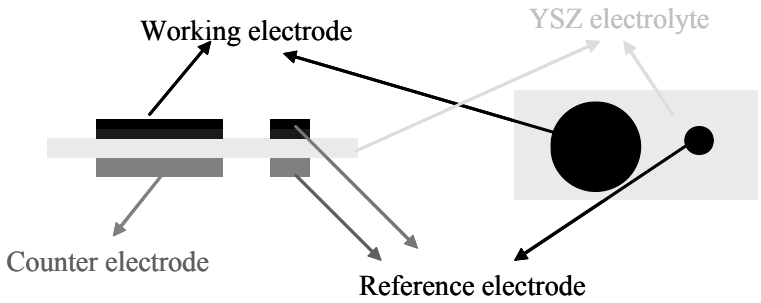

Figure 1. Diagram of the cell configuration for evaluating the electrochemical performance of oxygen evolution electrodes.

Three types of oxygen electrodes were made: (1) powder-based perovskite, (2) a layered structure of powdered perovskite on a sol-gel fine-grained PSC layer, and (3) a layered structure of powdered perovskite on a sol-gel PSC layer on a sol-gel CSO layer. The compositions of the powder-based perovskite electrodes were: $La_{0.8}Sr_{0.2}MnO_3$ (LSM), $La_{0.8}Sr_{0.2}FeO_3$ (LSF), $La_{0.7}Sr_{0.2}FeO_3$ (LSF-ns), $La_{0.8}Sr_{0.2}CoO_3$ (LSC), $Pr_{0.5}Sr_{0.5}CoO_3$ (PSC), and $LaNiO_3$ (LN). The perovskite powders were synthesized using the glycine-nitrate combustion synthesis process[3], pressed into a pellet, and calcined at 1250°C for 1 h in air. The pellet was crushed into a powder and ball milled in ethanol for 1 week. The powder was then dried in air. Inks were made from the powders by mixing with ethanol—10g ethanol, 1.5 g powder—and ball milling for 3 days. The ink was then painted onto the YSZ or SSZ electrolyte substrates and fired at 1000°C for 1 h in air.

To improve the electrode performance by grading the grain size of the electrodes, samples of PSC were made with fine-grained layers at the zirconia interface and larger-grained layers at the air interface. Because it is well documented that cobaltites react with zirconia in long-term tests, creating insulating phases,[4,5] interlayers of fine-grained doped-ceria were deposited at the zirconia-cobaltite interface of some of the samples. The fine-grained layers of PSC and $Ce_{0.8}Sm_{0.2}O_{1.9}$ (CSO) were made by sol-gel techniques to form films 0.1-3 μm thick on the electrolyte substrates. These nano-crystalline oxide films were synthesized by a polymeric precursor process developed by H. U. Anderson's group[6-8]. This

low-temperature process involved dissolution of metal nitrates in water, ethylene glycol, and polyvinyl alcohol. The nitrates were evaporated slowly on a hot plate at 80°C for approximately 24 h, with periodic additions of water to keep the volume of the solution constant, yielding a gelatinous, precipitate-free liquid. The polymeric precursor was then applied to the zirconia electrolyte substrates by dipping in the CSO gel or painting on the PSC gel. The films were dried at 80°C for 30-60 min and subsequently annealed at 400°C for 1 h or more. The process of applying the gel and firing was repeated 10 times for the CSO gel and 5 times for the PSC gel to obtain continuous, fine-grained layers. After this, powder-containing ink was painted on top of the sol-gel layers and fired at 1000°C for 1 h. After the final firing, the powder layers were approximately 10 μm thick and the sol-gel layers 0.1-3 μm thick.

Electrochemical Evaluation of SOEC Electrode Materials

The electrochemical performance of the oxygen electrodes was evaluated in air in a single-atmosphere test apparatus at temperatures from 700 to 1000ºC. The oxygen electrode performance was evaluated using AC impedance spectroscopy (Princeton Applied Research 273/273A potentiostat/galvanostat with a Solartron 1255 frequency response analyzer) in both controlled current and controlled potential modes. For the controlled current mode, the anodic DC polarization was 4.1 mA and the AC signal amplitude was 4 mA. For the controlled voltage mode, the anodic DC polarization was 10 mV and the AC signal amplitude was 10 mV. Impedance data were taken during increasing and decreasing temperatures.

Calculation of SO_2 Yields of SO_3 Electrolysis Cells

The traditional oxide ion-conducting electrolyte for both steam electrolysis cells and solid oxide fuel cells is yttria-stabilized zirconia (YSZ). This material has high oxide ion conductivity at temperatures >900ºC. However, the desired operating temperature for the proposed SO_3 electrolysis cell is <600ºC, preferably 500ºC. At this temperature, the conductivity of the YSZ electrolyte is approximately two orders of magnitude lower than at 1000ºC,[10] which would either severely limit the SO_3 electrolysis rate or result in unacceptably high cell voltages. Scandia-stabilized zirconia (SSZ), gadolinia-doped ceria (CGO), and lanthanum strontium magnesium gallate (LSGM) have higher oxide ion conductivity at 500ºC than does YSZ at similar temperatures.[9-11] The SO_2 yields of these four electrolyte materials with thicknesses varying from 10 μm to 500 μm and at temperatures varying from 450°C to 600°C were calculated using the following equation:

$$SO_2 \text{ production rate (mol/s-cm}^2) = [(V\sigma/t)/nF]$$

where V is the cell voltage increase caused by the impedance of the electrolyte to the conduction of oxide ions (chosen to be 0.5V), σ is the oxide ion conductivity of the material at the given temperature in S/cm, t is the electrolyte layer thickness in cm, n is the number of electrons transferred per molecule of SO_2 produced (n=2), and F is the Faraday constant in coulombs/mol (or A-s/mol).

Phase Stability of SO_3 Electrolytes

As stated above, four materials were identified as candidate electrolytes for the SO_3 electrolysis cells: YSZ, SSZ, CGO, and LSGM. Thermodynamic analyses of the stability of these materials' constituent oxides at 500–600°C in SO_3/SO_2 atmospheres were performed using a commercially available thermodynamic software package, HSC Chemistry©.[12]

The stability of these four candidate electrolyte materials in an SO_3 atmosphere was also determined experimentally by exposing powdered samples of these materials to an SO_3-containing atmosphere at 500°C for 24 h and cooling the samples to room temperature in

argon. The partial pressure of SO_3 in the argon carrier gas was calculated to be 0.6 atm. The starting compositions of these materials were $Ce_{0.8}Gd_{0.2}O_{1.9}$ (CGO, Praxair), $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ (LSGM, Praxair), 10 mol%Sc_2O_3-1 mol%CeO_2-89 mol% ZrO_2 (SSZ, Daiichi Kigenso), and 8 mol%Y_2O_3-92 mol%ZrO_2 (YSZ, Aldrich). The exposure experiments were performed twice for the YSZ and LSGM samples. During the second additional exposure experiment, the YSZ and LSGM samples were exposed to SO_3 at 500°C for 2 hours and cooled to room temperature in the SO_3 atmosphere. The powder samples were analyzed for their phase composition before and after exposure to SO_3 by X-ray diffraction analyses (XRD). The sensitivity of XRD to detect minority phase was approximately 5 mol%.

Results and Discussion

SOEC Oxygen Electrode Development

A summary of the electrode impedances of the powdered perovskite samples is presented in Figure 2, as the area specific resistance (ASR or area-normalized impedance). The data shown are the best of two or three samples tested for each composition. The differences between multiple samples of each composition were likely due to differences in contact between the perovskite electrode and zirconia substrate. These results show that the cobaltites, ferrites, and the nickelate all have improved performance for oxygen evolution compared with the standard manganite material. The performance of the cobaltites and nickelate is comparable. The best oxygen evolution performance (i.e., lowest electrode impedance) was obtained with the non-stoichiometric lanthanum strontium ferrite ($La_{0.7}Sr_{0.2}FeO_3$). For all of the powdered perovskite test electrodes, the ASR values showed Arrhenius behavior. The ASR values determined during the increasing temperature profile were higher than those on the decreasing temperature profile (i.e., exposure of the electrodes to 1000°C improved their performance). This improvement in catalytic activity could be due either to altering the microstructure or to the effect of current-conditioning-like enhancement during the multiple polarization measurements at each temperature. It is important to note that the microstructure of the powdered perovskite samples that we tested was not optimized.

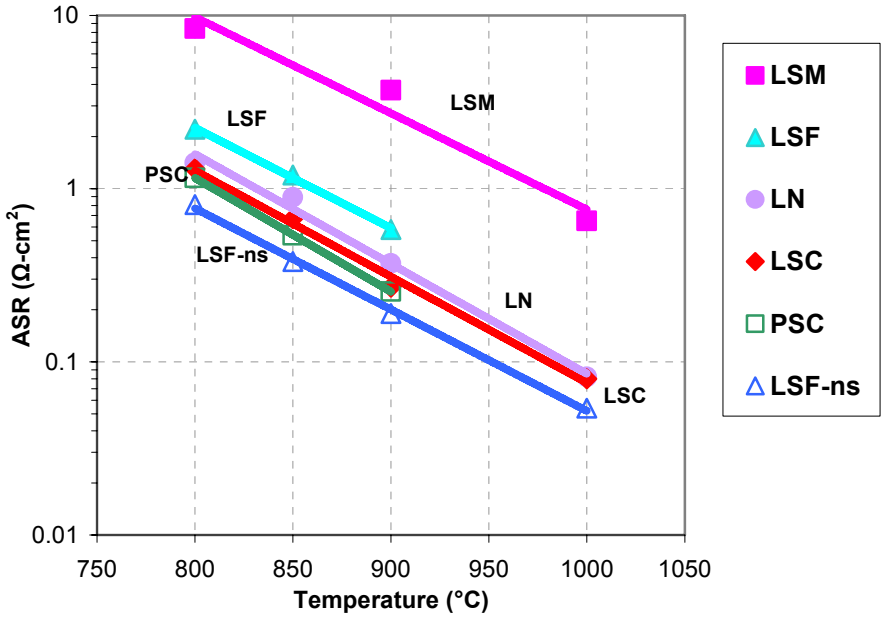

Figure 2. Temperature dependence of ASR for the powdered perovskite electrodes.

We used the PSC composition for the samples with fine-grained layers because we were unsuccessful in making a precipitate-free LSF-ns sol-gel. The samples consisting of a PSC sol-gel thin-film interlayer deposited on the SSZ substrate followed by PSC powder ink painted on the PSC sol-gel interlayer will be denoted by PSC/PSC gel/SSZ. The samples consisting of a CSO sol-gel interlayer deposited on the SSZ substrate followed by a PSC sol-gel interlayer deposited on the CSO sol-gel interlayer followed by a PSC powder ink painted on the PSC sol-gel interlayer will be denoted by PSC/PSC gel/CSO gel/SSZ or PSC/PSC gel/CSO gel/YSZ. The results of the impedance tests are shown in Figure 3. All of the data shown were taken during decreasing temperature profiles, even though the two samples with CSO interlayers had higher ASRs in the decreasing temperature profile compared with the increasing temperature profile. It can be seen in Figure 3 that the best PSC/PSC gel sample was not better than the PSC powder alone. However, the samples with ceria interlayer were both significantly improved, especially at lower temperatures. The improved performance of the electrodes with the CSO interlayer can be attributed to the role of CSO in preventing the reaction of the strontium in the electrode with the zirconia in the electrolyte to form insulating strontium zirconate.[4,5] It should also be noted that impedance of this type of electrode was lower on the YSZ substrate than on the SSZ substrate. The reasons for this difference are unknown.

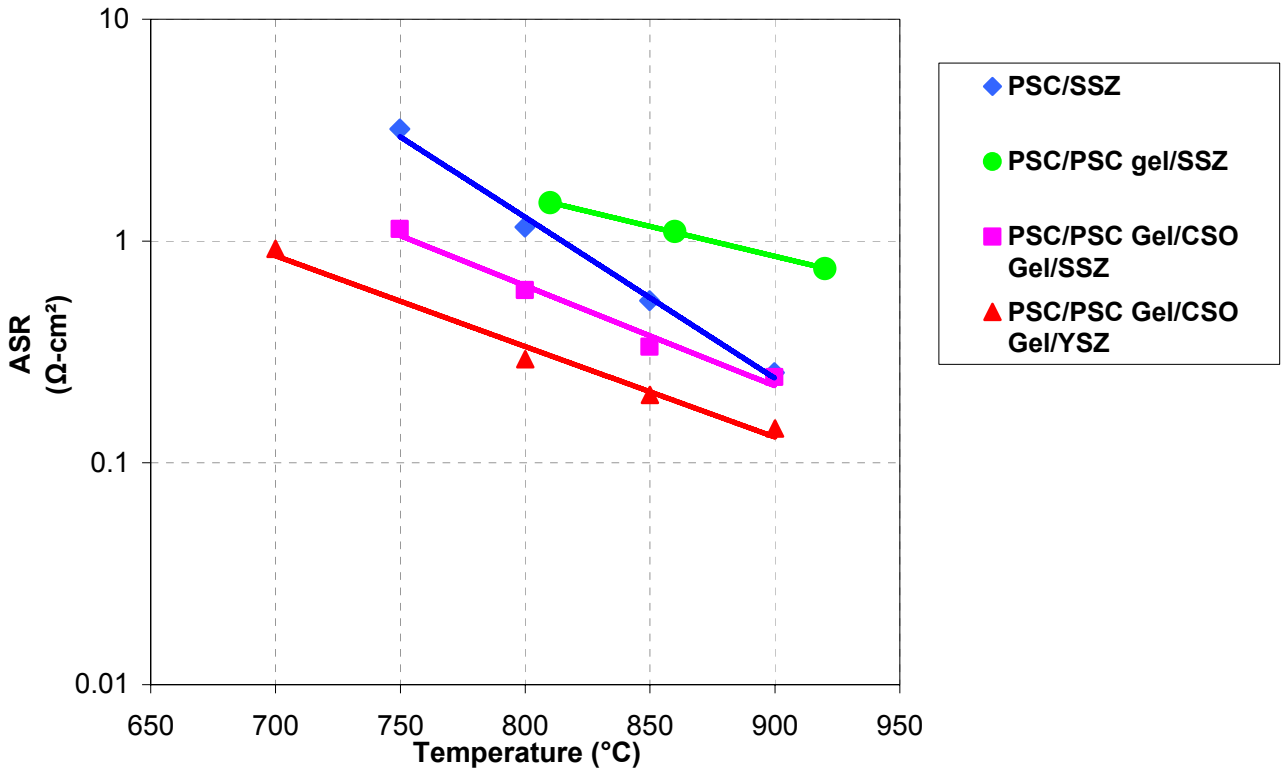

Figure 3. Temperature dependence of ASR for PSC electrodes with and without fine-grained interlayers.

Thermodynamic Analyses of SO_2 Yields of Electrolysis Cells

The calculations illustrated in Figures 4 and 5 show that the SO_3 to SO_2 conversion rate per unit area of cell could be increased by factors of 2.1, 4.8, and 12.6 by replacing YSZ, with SSZ, CGO, or LSGM electrolyte, respectively. These calculations also show that SO_3 conversion rates could be increased dramatically by using a thin electrolyte supported on a thick electrode or bi-polar plate, possibly allowing a decrease of the electrolyte layer thickness by at least an order of magnitude (i.e., from >100 μm down to 5–10 μm).

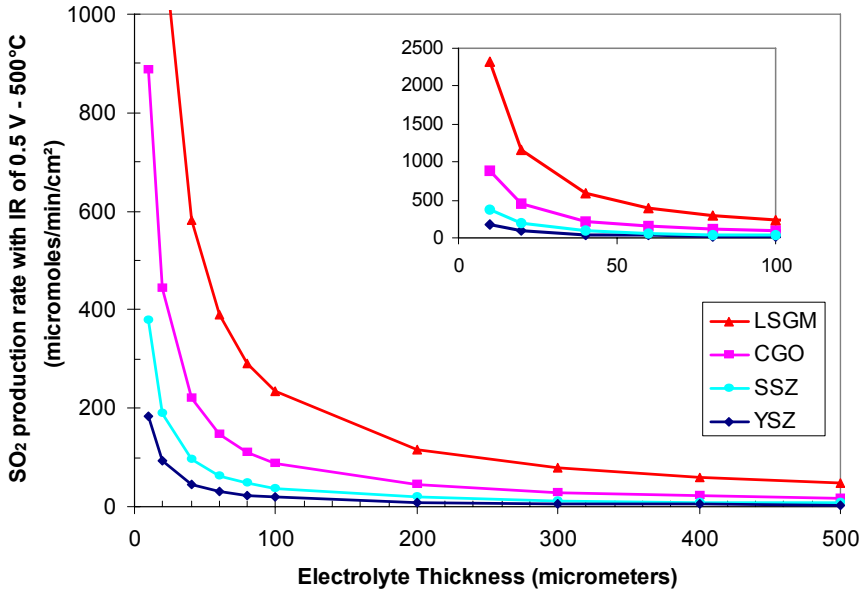

Figure 4. SO_2 production rate at 0.5 V electrolyte overpotential and 500°C, as a function of thickness for YSZ, SSZ, CGO, and LSGM electrolytes.

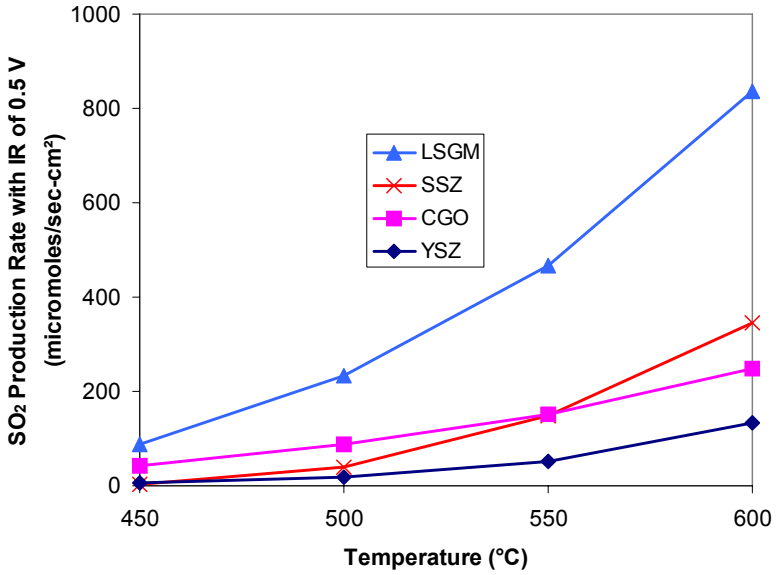

Figure 5. SO_2 production rate as a function of temperature for a 100-μm-thick electrolyte and 0.5 V overpotential for YSZ, SSZ, CGO, and LSGM electrolytes.

SO_3 Electrolyte Phase Stability Studies

An example of a phase stability diagram arising from our thermodynamic analyses using HSC Chemistry© is shown in Figure 6 for zirconia. The conditions encountered in the electrolysis cell would be high partial pressures of SO_3 and very low partial pressures of SO_2 at the inlet (upper left corner of the predominance diagrams of Figure 6). The conditions at the outlet would be the reverse and are represented in the lower right region of the predominance diagrams. These plots show that ZrO_2 is the thermodynamically stable phase under all SO_3/SO_2 ratios at 600°C. However, at 500°C, zirconium sulfate is the stable phase at SO_3 partial pressures greater than 0.158 atm. The concentration of SO_2 has no effect on phase stability at these temperatures. Further analyses were performed to define the temperature boundary for the zirconium oxide to zirconium sulfate phase transition. It was determined that the thermodynamically favored phase is zirconium sulfate at all temperatures below 560°C when zirconia is exposed to 1 atm SO_3. The results of similar thermodynamic analyses of phase stability for the various candidate electrolyte oxides are summarized in Table 1. Based on these results, yttria-stabilized zirconia and scandia-stabilized zirconia are the preferred electrolytes for an SO_3 electrolyzer operating at 600°C in terms of stability. However, these zirconia-based electrolytes may react with SO_3 to form sulfates at temperatures below 560°C.

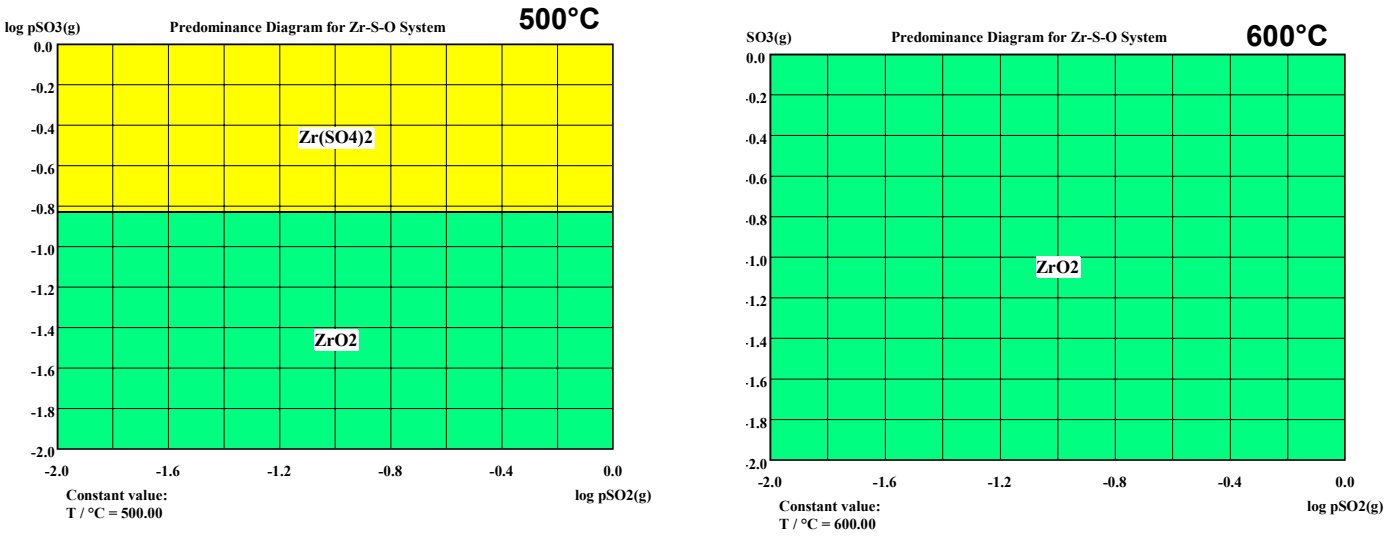

Figure 6. Predominance diagrams for zirconia at 500°C (left) and 600°C (right) in an SO_3/SO_2 atmosphere as a function of SO_3 (y-axis) and SO_2 (x-axis) partial pressures.

Table 1. Summary of thermodynamic calculations of oxide stabilities at 500°C and 600°C in SO_3 (pSO_3 = 10 mbar to 1 bar).

Oxide is stable, no reaction	Y, Ga, Sc, Gd
Reaction under some conditions	Zr
Sulfate is preferred phase under all conditions	Mg, Sr, La, Ce

The results of the experimental SO_3 exposure tests of the various electrolyte materials were that CGO showed severe reactivity to form cerium and gadolinium sulfates and LSGM reacted slightly to form minor phases of strontium sulfate and lanthanum sulfate. The SSZ and YSZ showed no reactivity in the experiments where the sample chamber was purged with argon while being cooled to room temperature. The YSZ showed slight reactivity to form zirconium sulfate when cooled to room temperature in the SO_3 atmosphere. With two exceptions, the stability of zirconia at 500°C and the reactivity of gadolinia, these experimental results agree with the thermodynamic calculations.

Conclusions

SOEC Electrode Development

As oxygen evolution electrodes, the short-term performance of $La_{0.7}Sr_{0.2}FeO_3$, $La_{0.8}Sr_{0.2}CoO_3$, $Pr_{0.5}Sr_{0.5}CoO_3$, and $LaNiO_3$, even with non-optimized microstructures, is comparable to lanthanum strontium manganite LSM-YSZ composites.[13] The non-stoichiometric strontium-doped lanthanum ferrite, $La_{0.7}Sr_{0.2}FeO_{3,}$ was found to have the lowest area specific resistance of all electrodes tested. By engineering the microstructure of PSC, so that there were finer grains near the electrolyte interface and coarser grains at the air interface, and adding a doped-ceria interlayer between the zirconia electrolyte and PSC electrode to prevent the formation of insulating secondary phases, improved ASRs were achieved.

SO_3 Electrolyte Studies

The electrolysis of SO_3 to SO_2 using an oxide ion-conducting solid oxide electrolyzer is a promising approach to reducing the maximum temperature needed for the sulfuric acid thermochemical hydrogen production cycle from 1000°C to 500–600°C. The stability of the oxide ion-conducting electrolyte in the reactive SO_3 atmosphere limits the choice of materials and may define the lower limit for the operating temperature of the electrolysis cell. Though the throughput of the cell could be enhanced by at least an order of magnitude by replacing the traditional oxide ion conductor, yttria-stabilized zirconia, with either gadolinia-doped ceria or lanthanum strontium magnesium gallate, these two materials were found to be highly reactive with SO_3, which may preclude their use in this application. The results of our thermodynamic calculations and our experimental stability tests indicate that scandia-stabilized zirconia may be a good substitute for yttria-stabilized zirconia and could increase the SO_3 conversion rate by a factor of two. However, the thermodynamic calculations indicate that zirconia-based electrolytes may only be stable in the SO_3 atmosphere at temperatures higher than 560°C. The most promising route for increasing the SO_3 conversion rate per unit area of cell is to reduce the thickness of the electrolyte layer from the conventional 100–150 μm to <10 μm by supporting the cell on a structural component other than a thick electrolyte (e.g., a thick electrode or bipolar plate).

Acknowledgements

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References

1. J. O'Brien, C.M. Stoots, J.S. Herring, and P.A. Lessing, *Fuel Cell Science, Engineering and Technology – 2004* (2004) 219-228.
2. T. Nakagiri, T. Hoshiya, and K. Aoto, "A new thermochemical and electrolytic hybrid hydrogen production process for FBR", *GENES4/ANP2003*, Sep. 15-19, 2003, Kyoto, Japan, Paper 1020.
3. L. A. Chick, L. R. Pederson, et al., *Materials Letters,* **10,** 1-2 (1990) 6-12.
4. J.M. Ralph, C. Rossignol, and R. Kumar, *J. Electrochem. Soc.,* **150**, 11 (2003) A1518-A1522.
5. H.Y. Tu, Y. Takeda, N. Imanishi, O. Yamamoto, *Solid State Ionics,* **117** (1999) 277-281.
6. H.U. Anderson, M. M. Nasrallah, and C.-C. Chen "Method of Coating a Substrate with a Metal Oxide Film from an Aqueous Solution Comprising a Metal Cation and a Polymerizable Organic Solvent." (1996) United States of America Patent No. 5,494,700.
7. B.P. Gorman and H.U. Anderson, *Journal of the American Ceramic Society*, **84,** 4 (2001) 890-892.
8. T. Suziki, I. Kosacki, and H.U. Anderson, *Solid State Ionics*, **151** (2002) 111-112.
9. Y. Arachi, H. Sakai, O. Yamamoto, Y. Takeda and N. Imanishai, *Solid State Ionics*, **121** (1999) 133.
10. K. Huang, R. S. Tichy and J. B. Goodenough, *J. Am. Ceram. Soc.,* **81**, 10 (1998) 2565.
11. S. Wang, T. Kobayashi, M. Dokiya, and T. Hashimoto, *J. Electrochem. Soc.* **147**, 10 (2000) 3606.
12. HSC Chemistry©, Version 5, Outokumpu Research. Oy, Pori, Finland, A. Roine.
13. M.J. Jørgensen, S. Primdahl, C. Bagger, and M. Mogensen, *Solid State Ionics*, **139** (2001) 1-11.