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Materials for hydrogen generation via water electrolysis

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Abstract A review is presented of materials that could be utilized as electrolytes (and their associated electrodes and interconnect materials) in solid-state electrolysis cells to convert water (or steam) into hydrogen and oxygen. Electrolytes that function as oxygen ion conductors or proton conductors are considered for various operating temperatures from approximately 80 °C to 1000 °C. The fundamental electrochemical reactions are reviewed with some discussion of special sources of steam and DC electricity (advanced nuclear) to drive the reactions at the higher temperatures.

Hydrogen generation via steam electrolysis

Hydrogen generation can be accomplished via water (steam) electrolysis at the cathode of cells utilizing solid membranes. The membranes typically are electronic insulators and gas-tight (hermetic), but conduct ions via fast diffusion through the solid. The cell combinations are generally categorized by the name of the solid electrolytes they utilize. It has been found for some operating fuel cell anode/electrolyte/cathode systems that the fuel cell reactions at the electrodes are reversible. However, reversibility has not been demonstrated for all cathode/electrolyte/anode combinations. The H_2O input can be liquid water at low temperatures or steam at high temperatures. Combinations of materials that are found in various types of solid electrolyte cells that likely could be used to generate hydrogen via electrolysis are described below.

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High-temperature inorganic membrane electrolyzers

High-temperature oxygen ion conductors

The most common high-temperature (e.g. approx. 800–1000 °C) cells being investigated are solid-oxide fuel cells (SOFCs) using yttria or scandia-stabilized zirconia electrolytes that are rapid oxygen conductors. Over many years, yttrium and scandium have been used to substitute on the zirconium lattice site to stabilize the cubic structure and increase oxygen ion diffusion by creating oxygen vacancies to compensate for their aliovalent (Y^{+3} or Sc^{+3} on Zr^{+4} site) charges [1]. Yttria provides excellent structural stabilization and good ionic conductivity. Scandia has been long known to provide higher ionic conductivity [2], but at additional material cost [3]. Loss of conductivity for scandia-stabilized zirconia has been reported [4] due to phase changes upon aging at high temperatures (i.e. 1000 °C). This instability certainly would be less of a problem for cells operated at the lower temperatures of this range (e.g. 800 °C). For long-life operation at high temperatures, it is very important to use suitable electrodes that don't interact (e.g. inter-diffuse) unduly with the electrolyte or lose their activity (e.g. sintering). Cells using zirconia electrolytes have traditionally used Ni–ZrO_2 and doped $LaMnO_3$ electrodes. These combinations have proven to be structurally and chemically stable at high temperatures for long periods of time with

fuel cells operating for up to 25,000 h with performance degradation of less than 0.1% per 1000 h [5]. Some inter-diffusion and formation of non-conductive compounds like $La_2Zr_2O_7$ has been reported [6], being more severe at high temperatures [7] and long times.

The electrolysis reactions to produce hydrogen using oxygen ion conductors are:

$$\text{Cathode: } H_2O + 2e^- = H_2 + O^{-2} \quad (1)$$

$$\text{Anode: } O^{-2} = 1/2O_2 + 2e^- \quad (2)$$

$$\text{Overall: } H_2O = H_2 + 1/2O_2 \quad (3)$$

During the electrolysis reaction, oxygen is removed from the electrolysis reaction site via the membrane (oxygen ion conductor), leaving hydrogen gas and any un-reacted steam on the cathode side. In order to obtain pure hydrogen gas, the hydrogen must be separated from the steam by using one of a number of methods. Methods could include condensation of the steam (followed by drying), or the use of a hydrogen conducting membrane (likely used at elevated temperature and perhaps elevated pressure).

Some of the earliest hydrogen production via high temperature steam electrolysis was carried out in Germany in the late 1970's using series-connected, tubular, zirconia-electrolyte cells [8]. Their designs (e.g. "HOT ELLY") included the possibility of using heat and electricity derived from a high temperature nuclear reactor to drive cells at high efficiencies [9, 10]. Reports from Germany on high temperature electrolysis [11, 12] continued through the mid-1980's, but construction of large-scale plants was never realized. This was partially due to the industrial extraction of hydrogen from inexpensive natural gas that was then available [13]. However, cell design may have been a factor since other electrolysis cell-stack concepts (e.g., series/parallel single cell tubes and planar stacks) were addressed in 1992 [14]. Subsequent testing of electrolysis cells utilizing tubular yttria-stabilized zirconia electrolytes in Japan was reported by Hino and Miyamoto [15]. There has been recent successful testing at INEEL and Ceramatec of planar-design, zirconia-electrolyte, solid oxide fuel cells as steam electrolyzers [16, 17]. Single cells and cell-stacks utilizing yttria and scandia-stabilized zirconia electrolytes were tested over a range of operating temperatures (700–850 °C) and steam/H_2 input compositions. Little activation polarization was observed near open circuit voltages. However, some activation polarization may have been masked by resistance dominated by a relatively thick electrolyte. Eguchi et al. [18] noted polarization losses due to concentration over-voltages at high temperatures when using Ni–YSZ electrodes. However, polarization is very sensitive to electrode microstructure (e.g. porosity) and can vary from study to study. The INEEL/Ceramatec data showed a linear and symmetric behavior in the *I–V* characteristics from the fuel cell mode to the electrolyzer mode of operation (up to the point of where steam is largely depleted). Cell degradation characteristics were at least as good in the electrolysis mode as in the fuel cell mode. However, longevity problems could likely be due to long-term corrosion and leakage (associated with cracking). These issues are tied to structural design and material selection. Loss of structural integrity of high-temperature steam-electrolysis cells after only one thermal cycle has been reported by Hino et al. [19]. Seal degradation due to corrosion and thermal cycling for these high-temperature devices is expected to be a large problem that must be overcome.

The proposed operating temperature for the zirconia membranes is within the 800–1000 °C range and therefore is a good match to utilize heat from a new generation of proposed high-temperature gas-cooled reactors [20, 21]. For instance, the Very High Temperature Reactor (VHTR) reference concept has been described as a helium-cooled, graphite moderated, thermal neutron spectrum reactor with an outlet temperature of 1000 °C or higher [22]. In the U.S. there are investigations to combine a nuclear reactor with a high temperature steam electrolysis plant to generate hydrogen. A schematic diagram of this combined plant is shown in Fig. 1. Process heat would be available for generating electricity and heating steam, after heat exchanging of the helium coolant, at outlet temperatures somewhat lower than the 1000 °C. The high temperature electrolysis utilizes both heat and electricity generated by the reactor. Another VHTR design, the Pebble Bed Modular Reactor (PBMR) is being developed in South Africa through a world wide international collaborative effort led by South Africa's Electricity Supply Commission (ESKOM, supplies approx. 95% of that country's electricity). The PBMR currently has an average helium coolant exit temperature of 900 °C under normal operating conditions [23].

Moderate-temperature inorganic membrane electrolyzers

Steam electrolysis is feasible at moderate temperatures using cells constructed with one of a variety of solid

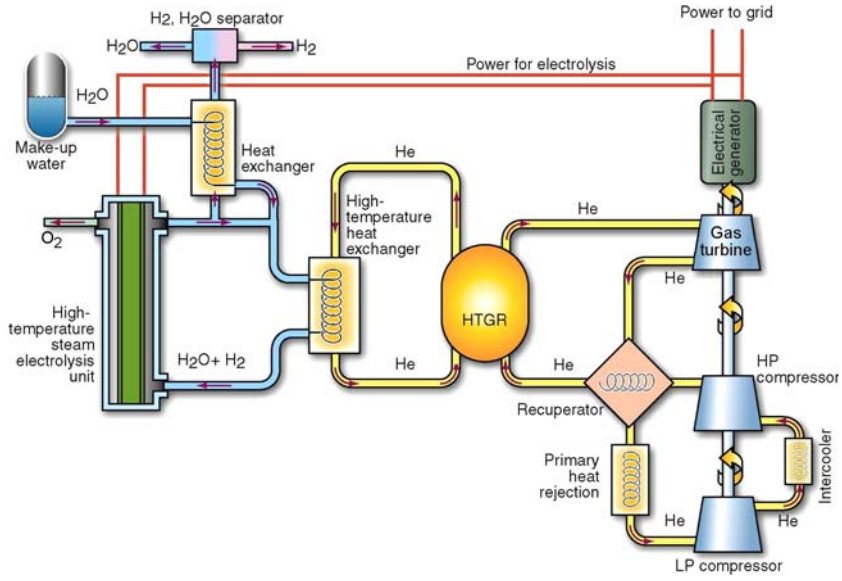

Fig. 1 High Temperature Steam Electrolysis to generate Hydrogen using heat and electricity from a Gas-cooled Nuclear Reactor

inorganic (ceramic) membranes. These temperatures could range downward from approximately 800 °C to about 500–600 °C using ceramic membranes that are either oxygen ion or proton conductors. This temperature regime is a good match to approximate coolant outlet temperatures that would be generated by various experimental nuclear reactor concepts [24], such as: Gas-Cooled Fast Reactor System (GFR) at 850 °C, Lead-Cooled Fast Reactor System (LFR) at 550 °C (perhaps up to 800 °C), Molten Salt Reactor (MSR) at 700 °C, Sodium-Cooled Fast Reactor System (SFR) at 550 °C, and Supercritical-Water-Cooled Reactor System (SCWR) at 550 °C. Of course the steam temperature in a secondary cooling loop would be somewhat less than a reactor's coolant outlet temperature due to heat-exchanger inefficiencies.

One approach to enable operation at lower temperatures is to reduce the thickness of zirconia electrolyte [25, 26] using any one of a number of diverse fabrication techniques such as: tape calendaring [27–29], centrifugal casting [30], sol-gel [31], vacuum plasma spraying [32, 33], reactive sputtering [34], pulsed laser-plasma evaporation [35], chemical vapor deposition (CVD) [36], or electro-chemical vapor deposition (EVD) [37]. Very thin electrolytes generally have to be supported by a thicker, porous electrode. Wang [19] mentions the problem of micro-porosity that is normally observed in zirconia electrolytes when using the evaporative-type deposition techniques, whereas CVD-type coatings are generally much more hermetic. The other approach is to develop new electrolyte compositions with higher ionic conductivities (for a given temperature range). Even though these electrolytes have higher ionic conductivities than zirconia at temperatures in the 600–800 °C range, they generally haven't been applied at higher temperatures for a variety of reasons: (1) Low activation energy for diffusion such that, while ionic conductivity is higher than zirconia at moderate temperatures, ionic conductivity can be lower than zirconia at high temperatures, (2) chemical instabilities, inter-diffusion, or reactions with other cell components (electrodes, bi-polar plate, sealants), (3) poor high-temperature mechanical or creep properties, or (4) a desire to use the electrolyte in cell stacks in conjunction with low-cost metal bi-polar plates that operate best at low to moderate temperatures (due to problems with low-conductivity oxidation layers formed at high temperatures).

Over the last decade there has been significant R&D to reduce the operating temperature of solid oxide fuel cells. This primarily is intended to enable the use of cheaper, and higher conductivity (when compared to electronically conductive ceramics like doped lanthanum chromite) bi-polar plates made from metal alloys and at the same time minimizing formation of the low-conductivity metal oxide layers. This has spurred the trend toward fabrication of much thinner (e.g. films in range of 1–50 microns for reduced electrical resistance) electrolytes that are electrode-supported.

Moderate-temperature oxygen ion conductors

In the last few years, doped $LaGaO_3$ electrolyte has emerged as a fast oxygen ion conductor with low electronic conductivity that could be used at reduced temperatures (e.g. 600–800 °C). Aliovalent atoms are added to $LaGaO_3$ (ABO_3) in order to create large concentrations of oxygen vacancies. Typical ''dopants''

are Sr on the "A" site and Mg on the "B" site [38, 39] (LSGM) or occasionally Ba on the "A" site [40]. Other studies have been conducted to measure doped $LaGaO_3$'s electronic conductivity [41–43], and develop suitable electrodes [44–47]. Questions regarding $LaGO_3$'s high temperature strength, toughness/durability (compared to ZrO_2), and long-term interactions with electrode combinations are still being answered by single-cell fuel cell tests [48, 49]. Single-cells utilizing plasma-sprayed LSGM electrolytes have been recently reported by Ma et al. [50]. Because LSGM has a lower melting point than zirconia it may be easier to plasma spray gas-tight films using LSGM than when using zirconia. LSGM development has been slowed by its chemical reaction with nickel in the fuel electrode [51, 52]. Recently a CeO_2 (Sm doped) buffer layer has been added between the electrolyte and the fuel electrode that largely eliminates the reaction [53, 54]. Huang [55] notes greatly improved performance with $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSMCo) cathodes compared to LSM cathodes. A LSGM (strontium and magnesium doped $LaGaO_3$) electrolyte ("thin" film, anode supported) single-cell has been tested as an electrolyzer at 800 °C. The cell exhibited a steady current density of 700 mA/cm^2 for a period of 350 h [56]. Ishihara [57] has also reported doped $PrGaO_3$ is a fast oxygen ion conductor, but it doesn't seem to hold any advantage over $LaGaO_3$.

Doped ceria (CeO_2) has been a long-time oxygen-ion conducting SOFC electrolyte candidate [58]. Its ionic conductivity is about one order of magnitude greater than zirconia in the 500–600 °C range. Ceria hasn't been viewed as viable at high temperatures because of excess electronic conductivity. However, if the operating range is below 700 °C, then its ionic transference number is greater than about 0.9 and it could be considered as a candidate electrolyte for a moderate temperature electrolyzer. Typical dopants for CeO_2 are: Gd (10–20% substitution for Ce) [59], Y [60, 61], and Sm [62]. Materials cost for doped ceria electrolyte are significantly lower than for doped $LaGaO_3$ electrolytes [63].

With regard to electrodes, platinum's CTE is a good match to that of zirconia and doped CeO_2. Porous platinum is known to have excellent catalytic activity; but, due to high cost, platinum is usually used only in the developmental testing of some single-cells. Traditional conducting perovskite electrodes (air) have been developed with thermal expansion coefficients (CTEs) to approximate that of zirconia. Since ceria interacts too much with strontium-doped lanthanum manganites, other perovksites compositions have been proposed for air electrodes ($La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_{3-\delta}$ and $LaFe_{0.5}Ni_{0.5}O_{3-\delta}$) [64]. A strong need for alternative lower-temperature SOFC anodes to replace nickel cermets has not been clearly identified (although copper has been used to prevent carbon deposition when using hydrocarbon fuels). Ni has been shown [65] to exhibit the highest electrochemical activity for H_2 oxidation (and assuming reversibility, for H_2 reduction in an electrolyzer) of the group: Ni, Co, Fe, Pt, Mn and Ru. For operating fuel cells, over-voltages (polarizations) of Ni/samaria-doped ceria and Pt/samaria-doped ceria (SDC) cermet anodes were very small as compared with those of Ni/YSZ and Pt/YSZ cermet anodes. Electrode polarization generally is not a problem when operating at 950–1000 °C; however, polarization becomes a very significant problem at intermediate temperatures, especially for the air-electrode. A recent review of SOFC anodes by Jiang and Chan [66] is a good source for Ni/ZrO_2 information as well as for information on various other cermets or conducting oxides such as gadolinium- or samarium-doped ceria, titanate-base oxides, and lanthanum chromite-based materials. The Jiang and Chan article also reviewed thick, anode-supported and porous metal-supported thin-film electrolytes; where the porous support material provides the structural strength. Because of improved performance from the thin electrolytes, these type cells are being considered for operation in the 600–800 °C range. Since the porous support can have a significant thickness (e.g. in the 500–2000 μm range), polarization losses due to gas diffusion can become significant. Therefore, a graded pore size structure would become important with large pore channels to enable easy diffusion of gases in most of the electrode, yet have high surface area to enable the reaction near the electrolyte interface.

Bismuth oxide (Bi_2O_3) is a much better oxygen ion conductor than doped CeO_2 at intermediate temperatures and always has held promise as a high performance electrolyte. However, despite over 30 years of studies, Bi_2O_3 is still plagued with crystallographic and chemical stability problems that have prevented implementation in practical long-lived cells. As reviewed by Azad et al. [67], α-Bi_2O_3 (monoclinic) is stable below 730 °C while the very high conductivity δ-Bi_2O_3 (cubic, CaF_2 type) is only stable between 730 °C up to its melting temperature of 825 °C. This is much too narrow of a range that is too close to the Bi_2O_3 melting point. The δ-Bi_2O_3 contains 25% vacant oxygen sites that results in the extremely high oxygen ion conductivity (approx. 1 Ω^{-1} cm^{-1} near the melting point). The δ-Bi_2O_3 also must be phase-stabilized by doping (e.g. Y_2O_3) in order to avoid the cracking that results from the volume change associated with the

$\delta \rightarrow \alpha$ phase change. Even stabilized δ-Bi_2O_3 is prone to reduction into metallic bismuth (even at moderately low oxygen partial pressures). These features lead to the tentative conclusion that δ-Bi_2O_3 is not a good candidate to be an electrolysis cell's electrolyte. However, because of the promise of high conductivity at low to moderate temperatures, researchers in the 1990's studied a wide variety of bismuth oxide containing compounds. Because yttria-stabilized Bi_2O_3 will transform to a rhombohedral phase (via diffusion) when annealed at less than 700 °C [68], some research was conducted on rhombohedral-phase Bi_2O_3 that was stabilized by alkaline-earth oxide dopants (e.g. CaO–Bi_2O_3, SrO–Bi_2O_3, or BaO–Bi_2O_3) [69] or Nb_2O_5–Bi_2O_3 [70] which appeared to be more stable (remained as cubic phases) than Y_2O_3–Bi_2O_3.

During the 1990's a new group of low-temperature oxygen ion conducting compounds based on bismuth vanadate ($Bi_4V_2O_{11}$) were studied [71]. Crystal structures were studied into the mid-90's and it was found that $Bi_4V_2O_{11}$ exhibits three phases (α, β, γ) between room temperature and 800 °C. The γ phase is the high-temperature, highest oxygen conductivity phase due to anion vacancies and a disordering of the anion vacancies. The gamma structure can be stabilized to room temperature by partial substitution of various metal ions for vanadium. These compounds were termed BIMEVOX. Investigations of fabrication with possible application as an electrolyte with particular interested in copper substituted material (BICUVOX, e.g. $Be_2V_{0.9}Cu_{0.1}O_{5.35}$) [72] followed. There is some electrical conductivity data measured on BICUVOX ''cells'' [73, 74], but no actual fuel cell data seems to be available. This may be an indication of increased electronic conductivity [75] (electronic shorting of cells) or the material's dilation when this type of material is reduced in a hydrogen-containing atmosphere. For a depleted steam electrolysis gas stream, the H_2/H_2O ratio could be in the 0.85–0.90 range, which could cause reduction at the fuel electrode (cathode). At this time, BIMEVOX electrolytes could not be considered good candidates for moderate-temperature electrolytes for steam electrolysis cells.

Moderate-temperature proton conductors

Kreuer [76] has reviewed proton-conducting materials for fuel-cell applications, including both liquid and solid conductors. Using proton-conducting ceramics as an electrolyte for a steam electrolyzer involves the same reactions as for a low-temperature proton-conducting polymer membrane:

$$\text{Anode: } H_2O = 2H^+ + 1/2O_2 + 2e^- \quad (4)$$

$$\text{Cathode: } 2H^+ + 2e^- = H_2 \quad (5)$$

$$\text{Overall: } H_2O = H_2 + 1/2O_2 \quad (6)$$

Therefore, the proton conducting ceramics represent a significantly different technology than the oxygen ion conducting ceramics like zirconia, ceria, or lanthanum gallate. For fuel cell operations [77], the proton-conducting cells have a thermodynamic advantage over oxygen ion cells (due to product water being swept from the cathode by excess air required for cell cooling) and applications driven by maximizing efficiency at the expense of power density favor proton cells. Proton conductors like the cerates ($BaCeO_3$ and $SrCeO_3$) have been studied for a number of years, while doped barium zirconate ($BaZrO_3$) has been advancing strongly in the last couple of years due to reports of high conductivity and good chemical resistance to CO_2 (not relevant for steam electrolysis). Aliovalent acceptor doping (e.g. by Gd) of $BaCeO_3$ on the Ce site in compensated by the formation of oxide ion vacancies $V_O^{\bullet\bullet}$ to balance the site charges.

Water vapor in the cell can react with the oxygen vacancies to form protons per Eq. 7.

$$H_2O + V_O^{\bullet\bullet} + O_O^X = 2OH_O^{\circ} \quad (7)$$

The OH°_O specie is a proton bound to an oxygen ion in the lattice. However, the proton can hop from one oxygen ion to another, giving rise to proton conductivity.

Iwahara introduced [78] doped (Y, Yb, Sc) $SrCeO_3$ as a proton-conducting electrolyte with tests using platinum electrodes. He later reported [79] cell tests in both fuel cell and steam electrolyzer mode (for hydrogen production) using both platinum and nickel fuel electrodes. A small electrolyzer was fabricated using $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ electrolyte; and, pure and very dry hydrogen gas was produced [80] at 750 °C at the rate of about 3 L/h^{-1}. Emphasis later shifted to doped (Gd or Nd) $BaCeO_3$ because of increased proton conductivity [81, 82]. The temperature range of application for electrolyzers was anticipated by Iwahara to be 600–800 °C. There was some concern about the chemical stability of $BaCeO_3$ in CO_2 and H_2O. Even though $BaCeO_3$ dissolves in boiling water, it is relatively stable as a dense electrolyte at high temperatures in high water vapor atmospheres [83].

There has been considerable interest in developing proton-conducting perovskite ceramics in Germany. $BaZrO_3$ is a newly considered compound originated by Kreuer [84] for use in the 500–800 °C range. It is very refractory (good thermodynamic phase stability), and has good [85] proton conductivity if it is doped with acceptors (e.g. Y). Proton conductivity has been increased in $BaZrO_3$ grain boundaries by forming solid solutions with small amounts of $BaCeO_3$ [86]. Recently, electrical and mechanical properties were measured and fabrication techniques developed for barium calcium niobate ($Ba_3Ca_{1+x}Nb_{2-x}O_{0-\delta}$) [87, 88], but cell performance data is not yet available. Kreuer recently published a careful review of the considerations and problems involved with fabricating SOFCs utilizing proton-conducting perovskites [89]. The electrolyte thickness and electrodes have not been optimized for maximum performance. However, these materials have not shown sufficient conductivity to compete (in fuel cell or electrolyzer applications) with the best oxygen ion conductors until the temperature is less than about 700 °C.

Kobayashi et al. [90] conducted steam electrolysis experiments using $SrZr_{0.9}Yb_{0.1}O_{3-\delta}$ tubular electrolytes (2 mm walls) with platinum electrodes (cermet with the electrolyte powder) at low temperatures (460–600 °C) and was successful in generating hydrogen and oxygen. They used the low temperatures in an attempt to avoid excessive electronic (hole) conductivity in the electrolyte (they mention this temperature corresponds to the exhaust gas temperature of automobiles). As a result, the hydrogen production rate was relatively low (approx. 0.4 μmol min^{-1} cm^{-2} at 460 °C and 2.4 mA cm^{-2}). Their measured hydrogen production efficiency was about 35% less than theoretical (as determined by current) and was dependent upon the partial pressure of water vapor. This was attributed to the creation of electronic holes at the anode during operation and their subsequent conduction through the electrolyte to the cathode.

Moderate temperature bi-polar plates (interconnects)

At low to moderate temperatures new possibilities arise for using various metals as bi-polar plates. Most metals have too high (e.g. 15 E-6 $°C^{-1}$) of thermal expansion to match that of zirconia (10.5 E-6 $°C^{-1}$). In order to get a lower thermal expansion metals (to match zirconia) SOFC developers originally tried to use special high chromium alloys like 95Cr4–5Fe (''Plansee Alloy'') or 94Cr–5Fe–1Y_2O_3. However, they ran into the problem of high temperature Cr oxidation. The problem is primarily found on the cathode (air) side of a SOFC. At temperatures above about 800 °C, the predominant reaction is $Cr_2O_3 + 1/2O_2 \rightarrow 2CrO_3$ (high vapor pressure gas). The Cr must diffuse through the Cr_2O_3 protective coating such that Cr can continually evaporate as CrO_3 from the outer (exposed to air) surface at temperatures (some literature) beginning as low as 200 °C. Once in the vapor state, Cr condenses in the LSM fuel-cell cathode and at the LSM/electrolyte interface. One proposed mechanism is for Mn^{+2} ion to grab the oxygen from the CrO_3, resulting in precipitation of Cr crystallites [91]. However, if steam is available (cathode of electrolysis cell), thermodynamic calculations by Ebbinghaus [92] predict that oxyhydroxides of Cr such as $CrO_2(OH)_2$ and $CrO_2(OH)$ will predominate at temperatures below 800 °C. Kofstad and Bredesen [93] point out that a Cr problem may also exist at the anode (fuel) side of a SOFC if high water vapor partial pressures spur the formation and evaporation of chromium oxyhydroxides (e.g. CrO_2OH). This could be a problem for the cathode during operation at high temperatures as an electrolyzer because of the high water content.

The presence of alloying elements in the interconnect tend to minimize the tendency for the Cr oxidation to take place (especially after oxide scale formation). Alloy elements like Y, Ce, Hf, Zr, Al are reported to slow scale growth. However, these elements tend to form scales with low electronic conductivity, whereas Cr_2O_3 scales are semi-conductors. Yang et al. have reviewed the alloys being considered for SOFC bi-polar plates [94]. They present an evaluation of oxidation behavior that indicates chromia scales on chromia-forming alloys, especially the ferritic stainless steels, can grow to microns or even tens of microns thick after exposure for thousands of hours in the SOFC environment (even in the intermediate temperature range). They further state that this scale growth will lead to an area-specific resistance (ASR) that is likely to be unacceptable. Nonetheless, iron-based ferritic steels (BCC structure) are generally recommended because they have a reasonable CTE match to zirconia, and are less expensive are more easily fabricated than chromium-based alloys. Operating at the lower temperatures may help by slowing the evaporation and diffusion kinetics. The Cr issue is one of the primary reasons why SOFC developers are beginning to coat the air-side of the interconnect with various conducting-oxide diffusion barriers [95]. One issue is maintaining a thin but protective conductive scale (Cr_2O_3) on the air-side, the other issue is preventing the Cr evaporation and subsequent condensation reactions. In order to limit the growth rate of

Cr_2O_3 scale on the metal interconnect (minimize the electrical resistance at the surface) various ceramic (conductive) coatings have been applied on the air side of the metal interconnects. However, some inter-diffusion of elements between the protective coating and metallic interconnect has been observed to lead to non-desirable phases [96]. Most SOFC generator designs have non-cell components such gas inlet chambers or electrical leads that will be exposed to high temperature air where CrO_3 formation could be problematic. The use of alloys like Hastelloy S (67% Ni, 15.5% Cr, 15.5% Mo, 1% Fe, 0.02% La) and Haynes Alloy 214 could solve these problems. The Haynes alloy 214 is specifically designed for service in high temperature air at 900 °C and above. It is an alumina former that displaces Cr_2O_3 on the metal surface. The total Cr in the 214 alloy is only 16%, which could also reduce CrO_3 vaporization issue for non-stack structural elements. However, any substantial thickness of alumina coating may prove to have too high of electrical resistance.

Oxidation in H_2/H_2O mixtures could be a long-term problem for un-coated metallic bi-polar electrolyzer plates with low H_2 content gas. Horita [97] documents oxidation in Fe–Cr alloys using 1% H_2–Ar (balance) bubbled through water at 50 °C (approx. 10% H_2 content). A higher H_2 content and the use of coatings would greatly lessen this problem.

One solution to the interconnect oxidation problem has been developed at INEEL. It is to form a thin LSC coating (for low electrical resistance) on a porous NiAl plate [98, 99]. The NiAl is exposed to the fuel gas in a SOFC or hydrogen plus steam in an electrolyzer. There is some concern that the NiAl structural component will be slowly oxidized in hydrogen/steam mixture. Oxidation tests are being conducted at INEEL using 15% H_2 (minimum)/85% H_2O. One oxidation reaction possibility is: $2NiAl + 3/2O_2 \rightarrow 2Ni + Al_2O_3$. However, this probably won't cause significant conductivity problems because of the metallic Ni. Another possibility is a thin adherent coating of amorphous alumina within the open pores of the NiAl structure, but not a continuous coating. A non-continuous alumina layer should not pose much of a problem. The other reaction possibility would be: $2NiAl + 2O_2 \rightarrow Ni + NiAl_2O_4$ (spinel); this may present a problem, but there could be sufficient left-over nickel to preserve some electrical conductivity. Other intermetallics could be used that don't contain aluminum.

Other proposed solutions to interconnect oxidation can be found by searching patents. A ceramic plate (e.g. zirconia) with metal filled ''via'' holes extended through the thickness has been proposed by Hartvigsen [100], which is similar to a patent application by Badding [101]. For application at intermediate temperatures, the ''via'' filler material could be silver (m.p. = 962 °C) since silver oxide is not stable at high temperatures and silver is tremendously less expensive than platinum or palladium. A metallic interconnect plate with gas-tight, silver-filled, holes is described by Meulenberg [102] as providing lowered contact resistance at temperatures up to 800 °C. Wang et al. [103] describe sputter-deposited silver/yttria-stabilized zirconia cermets for electrodes as being ''stable'' at temperatures up to 750 °C. However, Stevenson [104] reported that silver was unstable (developed a large amount of porosity) when exposed to a dual atmosphere of H_2–3% H_2O on one side and air on the other side for 100 h at 700 °C. He found silver was stable when exposed to air for 100 h at 700 °C in an identical configuration. To reduce scale formation on the fuel cell interconnect, coating FeCrAl and FeCrMn(LaTi) alloys with nickel foils (dense, hot-laminated) has been studied at 800 °C in a 4% H_2–3% H_2O–Remainder Ar atmosphere [105]. These nickel foils seemed to be helpful in preventing oxide scales. In some cases a stable nickel aluminide layer was formed at the interface between the alloy and the Ni foil.

Low-temperature inorganic membrane electrolyzers

Electrolyzers operated at low temperatures don't take full advantage of thermodynamic efficiency advantages of operating at high temperatures. However, sealing bi-polar plate devices should be easier since thermal cycling would not result in high stresses due to thermal expansion mismatches between cell components and sealing material. Also, inorganic membranes will be more chemically stable in the 200–300 °C temperature range than most organic proton-conducting membranes. A typical pressurized water reactor [106] heats water from 285 °C to 306 °C (at 2150 psia) in its core and might be a heat source (heat-exchanged steam at temperatures significantly lower than the core temperature) for a low temperature electrolysis device.

Solid inorganic materials exhibiting fast proton conduction at low temperatures seem to be more prevalent than fast oxygen ion conductors. Some proton-conducting glasses achieve high proton mobility due to incorporation of water (bonded to POH groups). These glasses can be fabricated by sol-gel techniques at low temperatures. However, the gels are deliquescent and also are easily fractured into pieces when heated [107]. This limits the practical application of these glasses to very low temperatures and therefore limits the flux values of hydrogen that can be achieved.

Fabrication of proton-exchanged β''-alumina compositions is difficult because waters of hydration are lost during firing and therefore the crystal structure is irreversibly destroyed [108]. One approach used to solve this problem, for β''-alumina, has been to fabricate a potassium ion crystal structure by firing to high temperatures. Then, at room temperature, protons can be electrochemically ion exchanged into the crystals from a mineral acid [109, 110]. Since the potassium ion is larger than the sodium ion, using the potassium composition lessens lattice strain during the proton exchange process. In these oxide ceramics, two protonic species can exist. The first type is an H_2O molecule associated with a proton as a hydronium ion (H_3O^+). The second type is a proton bound to an oxygen ion of the crystal lattice ($=OH^+$).

Ion exchange techniques have also been applied to compositions of the family of three-dimensional sodium ion conducting ''NASICON''. NASICON is a three dimensional conductor, whereas β''-alumina is a two-dimensional conductor. NASICON membranes have primarily been used for efficiently producing caustic (NaOH) from concentrated sodium salts dissolved in water [111]. NASICON is a family of compositions; the original NASICONs were solid solutions derived from $NaZr_2P_3O_{12}$ by partial replacement of P by Si with Na excess to balance the negative charges to generate the formula $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$ ($0 \leq x \leq 3$). Work on NASICON fast Na^+ ion conductors reaches back to the 1970's with work by Goodenough et al. [112] with further elucidation of its conductivity [113–115], chemical durability [116], and thermodynamics [117] in subsequent years. NASICON compositions have been prepared by a sol-gel route, and then the membranes ion exchanged with hydronium ions [118]. However, severe difficulties with cracking of dense membranes occur during the ion-exchange [119]. Recently, a sintered proton-exchanged NASICON-type composition known as PRONAS™ has become available in experimental quantities from a commercial supplier [120]. This material was designed for use in liquid systems, but reportedly has been tested as a membrane for hydrogen gas separation. Presumably, the PRONAS™ composition was sintered and then proton-exchanged at room temperature; however, no chemical composition or processing details are available at this date.

Low-temperature pem-type electrolyzers

PEM fuel cells have been the subject of research and development for decades. In the 1960's NASA used PEM cells for their Hope, Gemini, and Biosatellite missions. After a lull in the 1980's, a rush of development began in the early 1990's for transportation applications. This was initiated by improvements in bonded-electrodes that enabled much higher current densities. When a reverse polarity is applied to a PEM fuel cell, the fuel cell reactions are reversed and become water electrolysis reactions (4,5,6, above).

The PEM cells typically use sulfonated polymers (e.g. Nafion™) electrolytes [121] that conduct the protons away from the anode to the cathode (in electrolysis mode). A complicating factor is that the solid-state conduction of the protons is accompanied by multiple water molecules $(H_2O)_nH^+$. Also, the membrane must be kept hydrated to sustain the conduction mechanism. Therefore, water recycling becomes a large consideration since water is constantly removed from the anode and reappears at the cathode (mixed with the hydrogen). At temperatures less than 100 °C, gaseous hydrogen is easily removed from liquid water but the hydrogen still contains water vapor that most likely requires dehumidification (e.g. pressure swing adsorption dryer). Electrodes generally have utilized finely divided platinum-black, or more recently IrO_2 or RuO_2 (for increased electronic conductivity) as catalysts [122]. Research is currently being conducted into PEM-type membranes that have better kinetics, yet are chemically stable, at elevated temperatures such that they could operate in steam [123].

PEM water electrolysis cells have a potential advantage over traditional low-temperature electrolysis cells (e.g. KOH in water electrolytes with palladium, titanium, or alternative metal or ceramic electrodes [124–128]) because PEM devices have been shown to be reversible. They can ''load-level'' by generating electricity from hydrogen (and oxygen) operating as a fuel cell when needed (peak) and reverse to operate as an electrolyzer by consuming electricity to produce hydrogen (and oxygen). This is convenient if excess electricity is available during low periods of consumption (off-peak) [129]. PEM electrolysis cells could also be used in hybrid systems utilizing solar energy [130].

Small (up to 240 SCF/h = 6 Nm^3/h) PEM electrolysis units are now available commercially [131] and efforts are being made to reduce their production cost [132]. Some critical attention to cell-stack lifetime must be paid in light of the degradation and thinning of Nafion™ 117 PEM electrolytes identified in long-term tests in Switzerland [133] (two 100 kW PEM water electrolyzer plants). The thinning process proceeded via dissolution of the membrane from the interface between the cathode and the membrane. The degradation rate depended upon the position within an

individual cell as well as the position of the cell in the electrolyzer stack. Oxidative degradation at the cathode may be related to a mechanisms such peroxyl-radical attack as described by in-situ spin trap electron paramagnetic resonance studies by Panchenko et al. [134].

Ando and Tanaka [135] have recently used a Nafion electrolyte in electrolysis mode to decompose two water molecules to simultaneously generate one molecule of hydrogen and one of hydrogen peroxide (used in paper/pulp and chemical industries). They do this by using a high applied voltage (1.77–2.00 V) in a two electron transfer process (cathode: $2e^- + 2H^+ \rightarrow H_2$ anode: $2H_2O \rightarrow HOOH + 2H^+ + 2e^-$) and a NaOH anolyte collection solution. No oxygen is generated.

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