SYSTEMETIC REVIEW OF NANO ELECTRODES FOR SOLID OXIDE FUEL CELLS

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ABSTRACT: Fuel cells offer several advantages over conventional routines of power generation, such as generously higher conversion efficiency, particular construction, negligible sitting restriction, what's more, much lower production of pollutants. Solid oxide fuel cell (SOFC), in principle, can utilize a wide range of ignition fuels including coal derived syngas (CSG).

I. INTRODUCTION

Nano scale materials (< 100 nm) are receiving increased interest for application in devices where their irregular properties may conceivably be exploited.[1,2] In solid oxide fuel cells (SOFCs) they can be added as impetus, where it has been theorized that the advantageous synergist properties of nano sized oxides relate to an enhanced surface opening concentration and increased ionic and electronic conductivities.[3-6] However, due to the elevated operating temperatures found in modern SOFCs, 500-750 °C, the use of entirely nanostructured components would undoubtedly lead to basic insecurity. Hence, nanoparticles have been incorporated related to more stable micrometer sized supporting practical architectures. The use of metal components in SOFC design has shifted system operating temperatures to 500-750°C, away from the ∼1000 °C systems at first adopted by Westinghouse and others. The penalty is that SOFC performance decreases fundamentally at these lower operating temperatures. Especially, it is the oxygen reduction reaction in the conventional SOFC cathode, a composite of LSM and YSZ, which is restricting at these intermediate temperatures. To enhance electrode performance at the lower operating temperatures, nano particulates are added to the internal surfaces of the permeable electrodes to enhance some aspect of the electrode processes. The nanoparticulates are commonly added through processes that involve the precipitation of a metal salt in the pores of the electrodes, and their subsequent decomposition, to generate the desired nano particulate metallic or oxide impetus. This method of electrode enhancement has proved reasonably successful. Also, it has been discovered that higher electrode loading of nanoparticulate impetuses further increases performance.
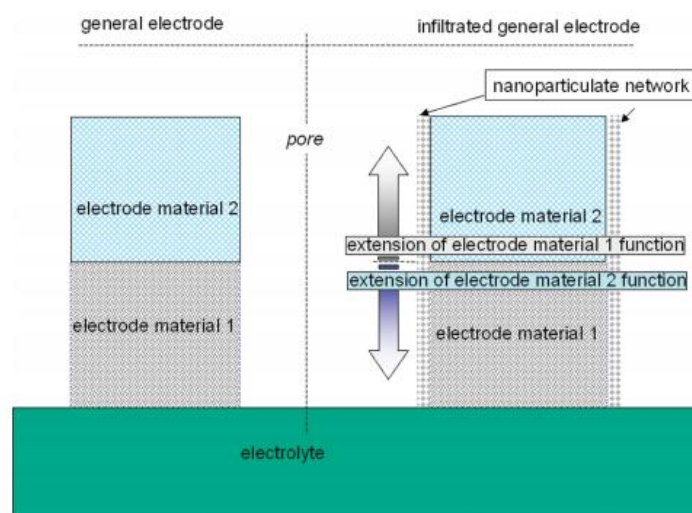

Figure 1. Cross-sectional illustration of nanoparticulate infiltration into a general composite electrode

II. LITERATURE REVIEW

The opportunities for SOFC technology just began with the Nernst's discovery of the solid-oxide electrolyte in 1899 (Minh and Takahashi 1995). 38 years later in 1937 the first SOFC was operated at 1000oC by Baur and Preis (Minh and Takahashi 1995). This first SOFC to be operated used ZrO2-based ionic conductors with iron or carbon as anode and Fe3O4 as cathode. In early 1960, serious development of SOFC began along two fronts: the two - cell arrangement and component materials.

Cell arrangement development started with a level plate design followed by a segmented-cell-in-series design by Bell and Spigot (Minh and Takahashi 1995), which was then modified by a banded setup. In 1980 seal less tubular SOFC was discovered, followed by solid SOFC two years later. At last the level plate design evolved due to advances in ceramic framing and processing technologies. These level plate and tubular cell designs are discovered to be the best cell arrangement today as appeared in Figure. 1.
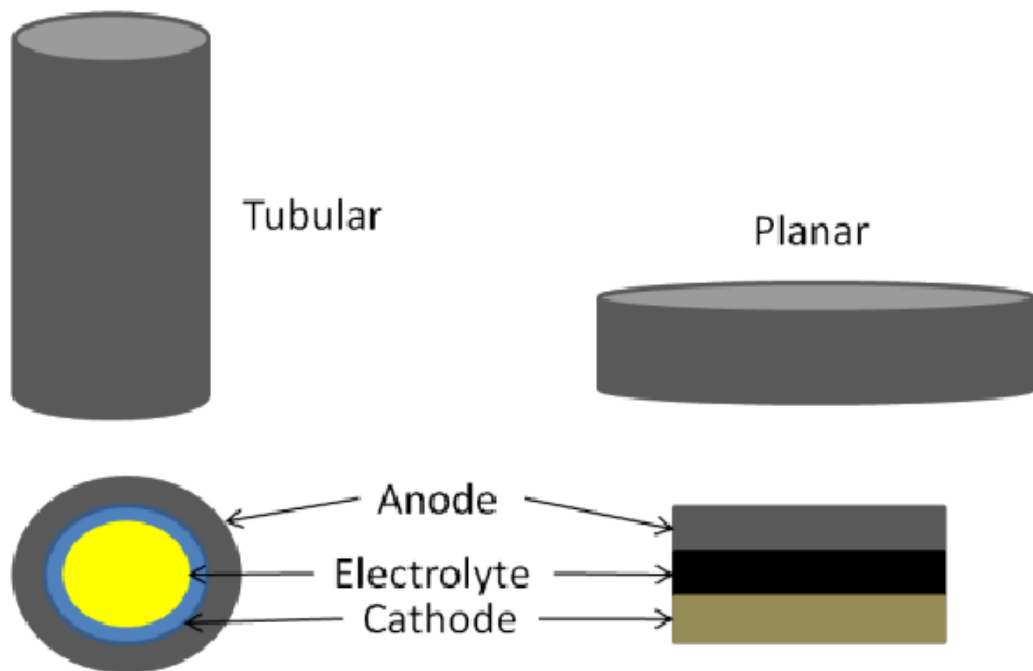
Figure 1. Tubular and planar design of SOFC

Cell design helps optimize surface contact between layers, consequently increasing the yield. The planar design has been discovered to be more capable of achieving very high power densities just as managing possible huge cost reductions through a concept called 'mass customization' – multi-stack fuel cells as the planar design is simpler and easy to fabricate into multiple layers (Singhal 2002).

The development of SOFC component materials, then again, began with the use of noble metals for electrodes and interconnects. The interconnect materials were replaced by LaCrO3 in 1980 and in conclusion by high temperature amalgams.

SOFC working Principles

A normal SOFC comprises of an oxygen particle conductor electrolyte, an air electrode (cathode) and a fuel electrode (anode). Air and fuel (normally hydrogen) is fed from cathode and anode sides respectively and are separated by the dense electrolyte layer. The difference in the oxygen halfway pressures in anode and cathode sides create a chemical potential difference over the electrolyte called the "open circuit voltage". This voltage is given by the Nernst equation which can be derived from the Gibbs free energy of the reaction of water development from oxygen and hydrogen as follows:

$\Delta G = \Delta G^o + RT\ln(K)$

$\Delta G = - \Delta W$ electrical $= - EQ = -nFE$

$-nFE = -nFE^o + RTln(K)$

$E = E^o + \frac{RT}{nF} ln(K)$

$K = \frac{pH2O}{pO2\ pH2}$

The conversion of this chemical energy to the electrical energy is realized when current is drawn from the cell. In this case, the oxygen molecules are reduced to oxygen particles at the cathode and afterward delivered to the anode side through the ionically conductive electrolyte. The oxygen particles delivered to the anode react with hydrogen to produce water and two electrons per oxygen particle (Figure 2.).
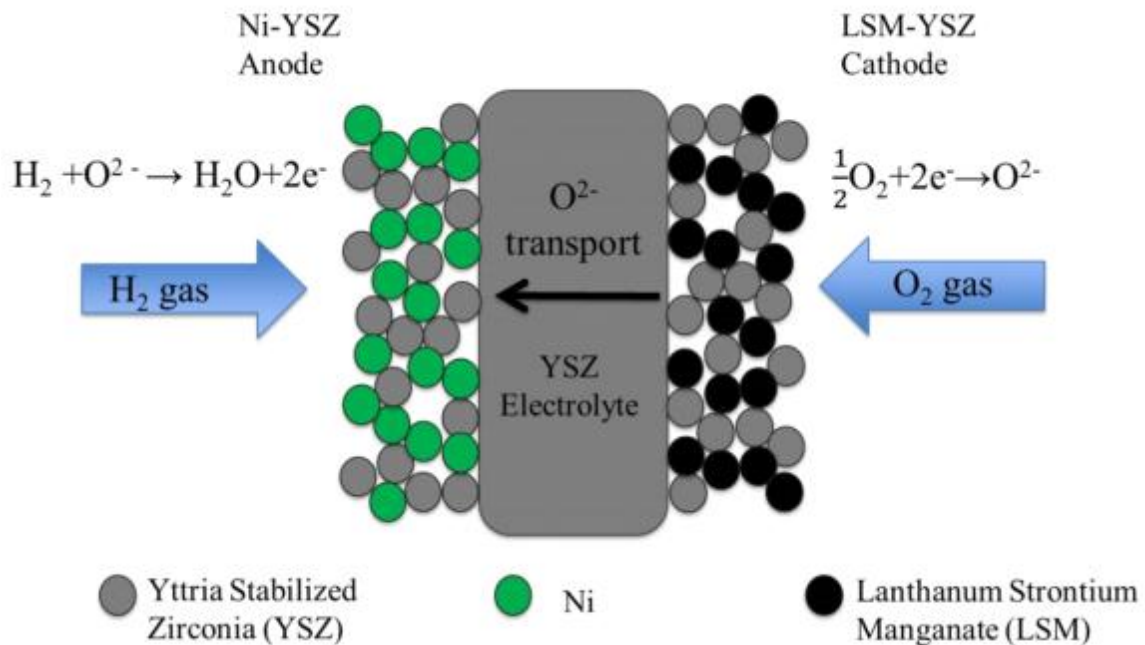

Figure 2. Schematic representation of a solid oxide fuel cell operation

Trace Impurities in Coal Derived Syngas

Coal syngas is derived from coal gasification process, a technique that converts the solid coal to be gas phase comprises of H2, H2O, CO, CO2, etc. In a gasification reactor, the coal is mixed with air with steam at high pressure (24-70 atm) and high temperature (500-1800oC) the essential reactions of the coal gasification are

$2C + O_2 = 2CO$

$C + H_2O = CO + H_2$

$CO + H_2O \Longleftrightarrow CO_2 + H_2$
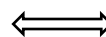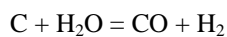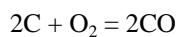
Table 1. Typical coal syngas composition

Component	Concentration (vol. %)
H2	30.6
CO	30.0
CO2	11.8
H2O	27.6

Among this process, the impurities existing in the coal will likewise be vaporized or gasified. The sum and the species of such impurities emphatically rely on the coal and the gasification process. Therefore, cleanup techniques like absorption, diffusion through a membrane; chemical conversion and filtering have been employed to remove some of the species like H2S, halides and fly debris particles. However, very few effective ways have been developed to remove other trace elements, for example, As, P, Zn, etc.

Despite the fact that the primary chemical arrangements and the concentrations of these trace elements can be understood, it is as yet not satisfactory what the real composition will be under SOFC working conditions. As the gas was heated to 800oC, it will be possible that the impurities react with the mass composition. Equilibrium gas phase calculation based on the lowest Gibbs free energy may offer such information. It has been reported that the same trace impurities have different chemical status at different temperatures.

Effects of Impurities on SOFC

The effects of the trace impurities in coal syngas on SOFC anodes have drawn a ton of attentions due to the motivation of direct utilization CSG as the fuel of SOFC. Thermodynamic equilibrium calculations have indicated that trace impurities species, for example, Be, Cr, K, Na, and V in the coal syngas structure condensed phases under warm gas cleanup conditions and can be effectively removed by the cleanup processes. Experimental results show that the existence of Hg, Si, Zn and NH3 in the coal syngas does not fundamentally affect the performance of the Ni-YSZ anode. The presence of Cd and Se in the syngas has impacts on the SOFC anode performance to some extent. Pollution species, for example, Cl, Sb, As, and P cause severe cell performance degradation due to assault on the Ni-YSZ anode. Sb, As and P have the potential to react with Ni to frame secondary phases in the Ni-YSZ anode, which deteriorate the synergist movement of the anode. The effects of specific impurities are described as follows.
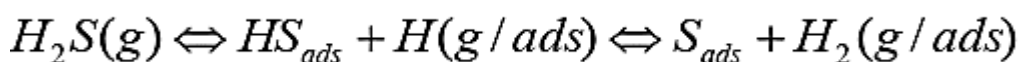
Sulfur

Sulfur is well known to have negative effects on the SOFC anode. The principle specie of S present in most convention fuel gas like flammable gas is H2S. It has been reported that CSG will contain 100-300 ppm H2S and in gaseous petrol the concentration will be higher than 1%. The detailed degradation mechanism has been proposed as follows

1.Physical absorption of H2S at the surface of the Ni-YSZ anode reduces the effective region for electrochemical reactions. This generally causes a fast degradation of the SOFC performance.

2.The absorbed H2S further reacts with Ni to frame Ni sulfide. This process reduces the electrochemical catalysis and reaction regions and causes a steady moderate loss of the performance.

The chemical reactions involved in this process will be:

$$H_2S(g) \Leftrightarrow HS_{ads} + H(g/ads) \Leftrightarrow S_{ads} + H_2(g/ads)$$

$$Ni + H_2S \Leftrightarrow NiS + H_2$$

$$3Ni + xH_2S \Leftrightarrow Ni_3S_x + xH_2$$

A significant phenomenon of the Sulfur harming effects is the self-recovery. Some researchers found if the H2S exposure time isn't long; the cell performance will be recovered when the fuel is switched back to clean fuel gas. A regular recovery plot is appeared in Figure 3.
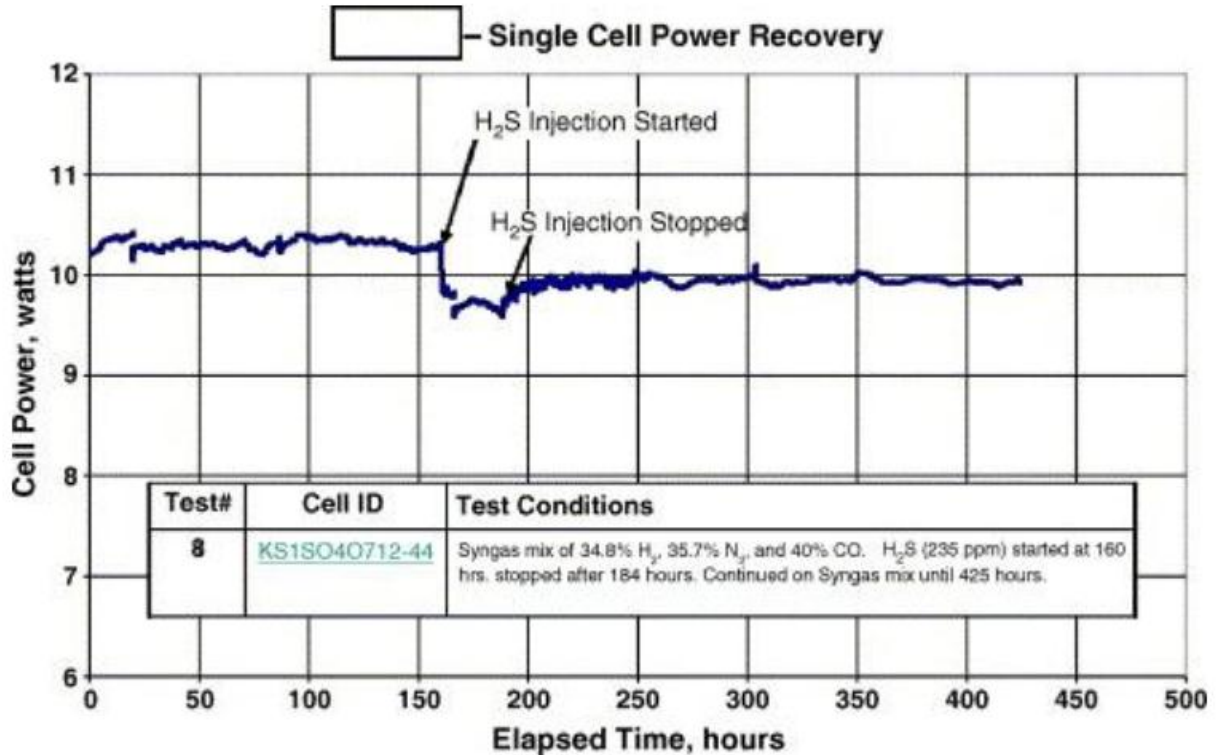

Figure 3. Sulfur poison recovery (Source: Trembly)

The primary reason for such recovery behavior is the removal of the surface adsorptive H2S, so the surface activation region can be revealed once more. Yet at the same time there are debates on this issue whether such process is reversible. Some sorts of Sulfur tolerant anode materials or electrode design strategies have been studied. Utilizing Cu-Ceria instead of NiYSZ or some perovskite ceramics as anode, some level of S tolerant properties have been found, however the performances are lower than traditional Ni-YSZ cermet.

Chlorine (Cl)

Chlorine is present in coal syngas in two significant structures: HCl and CH3Cl, both of the chemicals were used for evaluation the harming effect to Ni-YSZ anodes. Recently, Cl2 was likewise used with H2 on Ni-ScSZ (Sc stabilized Zirconia) anodes for investigating the degradation. It has been discovered that the degradation proportion depends on the operation temperature and the specie concentrations or even the current loads, and the observed results are not generally the same.

Arsenic (As)

Arsenic species could have different structures in coal syngas including AsH3, As2 and As4 depending on the gasification process. The degradation caused by introduction AsH3 to the fuel is chiefly because of the NiAs secondary phase formation which is less electronic conductive. Post exposure characterization reveals that as fundamentally located on Ni site which is consisted with thermal elements calculation as the NiAs composite is predicted.

Mercury

The mercury effects have relationship with the concentration. In lower concentration case (180 ppb), 750 and 800oC cells can stand, or even working better, however the degradation appeared at 850oC. For the higher concentration (7ppm), the degradation was likewise more serious at higher temperature (800oC) compared at 750oC. A possible reason is Ni and Hg framing low melting point eutectic composite.

Future Needs in SOFC Development

Significant technical difficulties in making SOFC commercially viable are the selection of materials and fuel cell producing (Yamamoto 2000). The selection is limited in large part by the imperatives imposed by the high SOFC working temperature of up to 1000oC on the selection of materials just as cell construction. The development of materials for SOFC components is based on (1) property similarity between neighboring components, (2) electronic and ionic conductivity of electrodes and electrolytes and (3) dependability in reducing and oxidizing environments.

III. CONCLUSION

Solid oxide fuel cells (SOFCs) are promising energy conversion devices due their high efficiency and fuel flexibility. SOFC will experience several redox (reduction-oxidation) cycles due to intentional or erroneous interruption of the fuel flexibly. Different techniques are used for the deposition of Pt electrodes including sputtering, chemical and electrochemical deposition. RF sputtering was applied to shape Pt anode and cathode layers in miniature solid oxide fuel cells.

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