

Novel Electrode Materials for Low-Temperature Solid-Oxide Fuel Cells

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ABSTRACT

Composite electrodes consisting of silver and bismuth vanadates exhibit remarkable catalytic activity for oxygen reduction at 500-550°C and greatly reduce the cathode-electrolyte (doped ceria) resistances of low temperature SOFCs, down to about 0.53 Ωcm^2 at 500°C and 0.21 Ωcm^2 at 550°C. The observed power densities of 231, 332, and 443 mWcm^{-2} at 500, 525 and 550°C, respectively, make it possible to operate SOFCs at temperatures about 500°C. Using *in situ* potential dependent FTIR emission spectroscopy, we have found evidence for two, possibly three distinct di-oxygen species present on the electrode surface. We have successfully identified which surface oxygen species is present under a particular electrical or chemical condition and have been able to deduce the reaction mechanisms. This technique will be used to probe the gas-solid interactions at or near the TPB and on the surfaces of mixed-conducting electrodes in an effort to understand the molecular processes relevant to the intrinsic catalytic activity. Broad spectral features are assigned to the polarization-induced changes in the optical properties of the electrode surface layer. The ability of producing vastly different microstructures and morphologies of the very same material is critical to the fabrication of functionally graded electrodes for solid-state electrochemical devices, such as SOFCs and lithium batteries. By carefully adjusting deposition parameters of combustion CVD, we have successfully produced oxide nano-powders with the size of 30 ~ 200 nm. Porous films with various microstructures and morphologies are also deposited on several substrates by systematic adjustment of deposition parameters. Symmetrical cells were fabricated by depositing cathode materials on both sides of GDC electrolytes.

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INTRODUCTION

Fuel cells have emerged as a leading technology to provide power sources in an efficient manner. Solid oxide fuel cells (SOFCs), in particular, have the potential to be among the cleanest, most efficient, and versatile technologies for energy conversion. When cleaned coal gas is used as the fuel, it can convert more than 55% of the energy in its fuel source directly to electricity. It is possible to reach 85% overall energy efficiencies when the high-quality waste heat from the electrochemical processes is recovered. SOFC emits no pollutants and as much as 65% less carbon dioxide (a greenhouse gas) than a conventional coal-burning plant.¹

It is the interfacial resistances that limit the performance of SOFCs at temperatures below 550°C. With continuous progress in fabrication of thin-film electrolyte membranes,² the performance of a new generation of solid-state fuel cells, the target system for SECA, will be determined essentially by the properties of the interfaces. To achieve the goals of the Vision 21 coal-based power plants or to enhance the performance of SOFC at low temperatures, the interfacial resistance of SOFCs must be dramatically reduced.

The objective of this project is to develop novel electrode materials for SOFCs to be operated at low temperatures in order to significantly reduce the cost of SOFC technology. More specifically, the technical objectives include

- To characterize the microscopic features of composite mixed-conducting electrodes and correlate with the ionic, electronic, and ambipolar transport properties as well as with the catalytic activities for pertinent electrochemical reactions;
- To gain a profound understanding of the principles of composite mixed-conducting electrodes, including simultaneous transport of ionic and electronic defects in the solid mixed conductor (influenced primarily by the defect structure), gas transport through the pores of the mixed conductor (influenced mainly by the pore structure), and the reaction kinetics at the mixed conductor/gas interface (influenced mostly by the surface structures and catalytic properties);
- To minimize interfacial polarization resistances through processing modifications, microstructure improvements, and new materials development

EXECUTIVE SUMMARY

We have successfully fabricated composite electrodes consisting of silver and bismuth vanadates, which exhibit remarkable catalytic activity for oxygen reduction at 500-550°C and greatly reduce the cathode-electrolyte (doped ceria) resistances of low temperature SOFCs, down to about 0.53 Ωcm^2 at 500°C and 0.21 Ωcm^2 at 550°C. The observed power densities of 231, 332, and 443 mWcm^{-2} at 500, 525 and 550°C, respectively, make it possible to operate SOFCs at temperatures about 500°C. While the long-term stability of the cathodes is yet to be characterized, the demonstrated remarkable performances (low interfacial resistances and high power densities) at low temperatures are very encouraging, implying that a new generation of low-temperature SOFCs is hopeful.

Significant reduction in operating temperature will dramatically reduce not only the cost of materials but also the cost of fabrication. It also implies greater system reliability, longer operational life, and increased potential for mobile applications. Low-temperature SOFCs have great potential to be affordable for many applications, including residential and automotive applications.

In situ potential dependent FTIR emission spectroscopy is capable of probing gas-solid interactions as electrochemical reactions take place under practical conditions for fuel cell operation, providing valuable information on surface chemistry and electrochemical processes of the cathodes without any modification. Using *in situ* pd-FTIRES we have found evidence for two, possibly three distinct di-oxygen species present on the electrode surface. Infrared is very sensitive to several forms of adsorbed oxygen, including peroxide ions O_2^{2-} (800-900 cm^{-1}), superoxide ions O_2^- (1040-1190 cm^{-1}), and adsorbed O_2 (1500-1700 cm^{-1}). We have successfully identified which surface oxygen species is present under a particular electrical or chemical condition and have been able to deduce the reaction mechanisms. This technique will be used to probe the gas-solid interactions at or near the TPB and on the surfaces of mixed-conducting electrodes in an effort to understand the molecular processes relevant to the intrinsic catalytic activity. Broad spectral features are assigned to the electrochemical-polarization-induced changes in the optical properties of the electrode surface layer. This, to the authors' best knowledge is the first report of infrared electro-emission.

The combination of *in situ* potential dependent FTIR emission spectroscopy (pd-FTIRES) and impedance spectroscopy (IS) will be a very powerful tool to investigate mechanisms of oxygen reduction, allowing direct correlation between the phenomenological behavior of an electrode (as determined by IS) and its surface molecular structures (as revealed by pd-FTIRES) under the actual fuel cell operating conditions. This will provide us with information that has never before been accessible, which is invaluable to rational design of better catalysts/cathodes for oxygen reduction. Further, the theory and methodology developed for study of cathodes are also being applied to study of anodes in order to achieve rational design of contaminant-tolerant anodes for SOFCs (to avoid carbon deposition and sulfur poisoning).

The ability of producing vastly different microstructures and morphologies of the very same material is critical to the fabrication of functionally graded electrodes for solid-state electrochemical devices such as SOFCs and lithium batteries. By carefully adjusting deposition parameters, we have successfully produced oxide nano-powders with the size of 30 ~ 200 nm. Porous films with various microstructures and morphologies are also deposited on several substrates by systematic adjustment of the deposition parameters. Symmetrical cells were fabricated by depositing cathode materials on both sides of GDC electrolytes.

EXPERIMENTAL

The most effective approach to creation of novel electrodes/interfaces of minimal resistance is to use porous mixed ionic-electronic conductors (MIECs) with mesoporous surfaces. MIECs^[3] allow simultaneous transport of both ionic and electronic defects, and the use of an MIEC as electrode may extend the active reaction sites from traditional triple-phase boundaries (TPBs) to the entire MIEC/gas interface, which can be orders of magnitude larger than the TPBs.^[4] The degree of this extension depends critically on the rate of defect transport through the solid MIEC, gas transport through the pores in the MIEC, and the catalytic activity of interfaces. While macro-pores (on the order of microns) promote rapid gas transport, meso- or nano-pores provide extremely high surface areas and high catalytic activity for electrode reactions. It is thus anticipated that macro-porous MIEC electrodes with meso-porous surfaces have great potential to re-define solid-state fuel cells at low temperatures. Successful creation of mesoporous MIEC electrodes with flexibility in composition and pore structure, and hence in electrical, transport, and catalytic properties, will create exciting opportunities in advancing not only low-temperature SOFCs but also other relevant systems such as membranes for gas separation, reforming of hydrocarbon fuels, and coal gas clean up.

Anode Materials: A suitable mixed-conducting anode material for SOFCs must be chemically, morphologically, and dimensionally stable in the fuel environment; have adequate electronic and ionic conductivity for charge and mass transport through the solid phase; have sufficient porosity to allow gas transport through the pores to or away from the reaction sites; have sufficient catalytic activity for electrochemical oxidation of the fuel; prohibit carbon deposition when hydrocarbon is used as fuel; be chemically and thermally compatible with other components; and be easy to fabricate and inexpensive.

Cathode Materials: Our recent exploration of new cathode materials indicates that $\text{Sm}_x\text{Sr}_{1-x}\text{CoO}_3$ (SSC) is very active for oxygen reduction at low temperatures (400-600C). The resistance of an SSC-SDC interface was less than $0.07 \text{ Ohm}\cdot\text{cm}^2$ at 600°C .^[5] We would like to systematically investigate into the SSC family of materials, including doping of other impurities, addition of a second phase to form composites, and synthesis and processing of these materials as meso-porous coatings for surface modification. The general guidelines outlined for microstructural design of anode is also applicable to the microstructural design of cathodes.

Microstructures: The overall performance of a composite electrode is greatly influenced by the microstructures of the electrode and the electrolyte-electrode interfaces, including the volume fraction and distribution of each phase (metal and ceramic), grain sizes and connectivity of each phase, as well as porosity and specific surface area. For example, the transport of gas (oxygen, fuel, and reaction products) to or away from the active sites is greatly affected not only by the open porosity but also by the microstructure such as size, shape, and distribution of pores in the electrode. Our recent studies indicate that, in order to optimize electrode performance, the electrode should have a porosity of $\geq 30\%$, specific area of $\geq 50 \text{ m}^2/\text{g}$ and high catalytic activity.

RESULTS AND DISCUSSION

Composite cathodes consisting of Ag and $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{0.1}\text{O}_{5.35}$ (BICUVOX.10) were prepared and characterized in a low-temperature SOFC based on a GDC ($\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$) electrolyte. The cells were fabricated by a dry-pressing process and sintered at 1350°C for 5 hours,^[6] resulting in a dense GDC film (about $30\ \mu\text{m}$ thick) on an GDC/NiO substrate. Shown in Figure 1 are the cathode-electrolyte interfacial resistances as a function of cell operating temperature, together with the total cell resistances and the electrolyte resistances. The interfacial resistance between the Ag-BICUVOX cathode and the GDC electrolyte at 500°C is only about $0.53\ \Omega\text{cm}^2$, much smaller than those of the LSCF-GDC ($\sim 10\ \Omega\text{cm}^2$)^[7], SSC-SDC ($\sim 1\ \Omega\text{cm}^2$)^[3], or SSC/GDC ($\sim 1\ \Omega\text{cm}^2$)^[8] cathode. The interfacial resistance of the Ag-BICUVOX cathode may be further reduced since the electrochemical performance of a composite cathode can be significantly improved by optimizing their microstructures and composition^[9,10] Shown in Figure 2 are the current-voltage characteristics and the corresponding power densities for a fuel cell using the Ag-BICUVOX cathode. Each datum point was recorded about 30 min after the cell reached a steady state. Maximum power densities were 130, 231, and $443\ \text{mW}/\text{cm}^2$ at 450, 500, and 550°C , respectively. The observed current and power densities at temperatures around 500°C represent the highest performances ever reported in the literature for SOFCs operated at these temperatures.

Electrodes for honeycomb cells based on YSZ have also been developed. The cathode is a composite consisting of silver and yttria doped bismuth oxide (YDB), which is an excellent oxygen ion conductor. YDB was synthesized using a co-precipitation method. Silver oxide was then mixed with YDB by ball milling with organic binders and acetone to form slurry, which was subsequently coated onto the inner channels of YSZ honeycombs. The coated layers were then dried, fired, and characterized in air using impedance spectroscopy. Shown in Figure 3 are several impedance spectra of a Ag-YDB composite electrode measured in gases containing different partial pressure of oxygen at 600°C . Shown in Figure 4 are the interfacial polarization resistances of several cathodes (as determined from the impedance spectra) including a Ag-YDB composite,^[11] a recently developed functionally graded cathode,^[12] and a composite consisting of lanthanum strontium manganite (LSM) and gadolinium doped ceria (GDC).^[13,14] Clearly, the polarization resistances of the Ag-YDB composite cathode are far smaller than those of other cathodes.

Potential dependent Fourier transform infrared emission spectroscopy (pd-FTIRES) has been used for the first time to study, *in situ*, oxygen reduction under practical operating conditions of intermediate-temperature solid oxide fuel cells (SOFCs). Figure 5 shows a schematic diagram of the optical configuration used for the emission measurements. The spectroelectrochemical cell was placed on the top of the sample cup in a Praying MantisTM diffuse reflectance sampling accessory equipped with a high temperature reaction chamber. The Praying Mantis attachment was positioned at an emission port on the Bruker Equinox 55 FTIR spectrometer. The top surface of the electrode ($0.13\ \text{cm}^2$) then becomes the source of infrared light modulated by the interferometer. While the transfer optics are not perfectly optimized, the

electrode surface is at the focal point of the ellipsoidal optics in the diffuse reflectance attachment and the f number for the focusing mirror in the emission port is small, therefore light levels reaching the detector are high enough for high quality spectra.^[15] The electrochemical cells investigated in this study were based on samaria-doped ceria (SDC) electrolyte and samarium strontium cobalt (SSC) oxide electrodes. Symmetric cells (SSC/SDC/SSC) were used for simplicity, the cathode acting as the IR emitter and the oxygen-generating anode serving as the counter electrode. Surface emission difference spectra of functioning cathodes at 550°C under a variety of feed gas conditions and overpotentials were obtained. Shown in Figure 6 are the pd-FTIRES spectra recorded for a symmetric cell, SSC/SDC/SSC, in air, 1% oxygen, and in N₂ for various applied potentials. The local baselines have been corrected with cubic polynomial fits between 1435 and 830 cm⁻¹. This was done to separate out the electro-emission effect from the adsorbate mode changes. As a comparison of the three stack plots indicates, changes in partial pressure of oxygen and the cathodic overpotential induced remarkable spectral changes. The pd-FTIRES spectra obtained at 550°C under cathodically polarized conditions showed a very strong absorption band at about 1124 cm⁻¹ and two weak absorption bands at 1236 cm⁻¹ and 930 cm⁻¹ (near the high-frequency tail and low frequently tail of the 1124 cm⁻¹ band), respectively. The strong band at 1124 cm⁻¹ and the weak band around 1236 cm⁻¹ are assigned to normal and perturbed superoxide ions (O_2^-), respectively.^[16] The weak band around 930 cm⁻¹ is assigned to peroxide ions (O_2^{2-}), again based on analogous assignments in the literature. The interactions between superoxide ions and the electrode surface, as revealed by *in situ* pd-FTIRES, are very sensitive to the local oxygen concentration. The interfacial structural data were also correlated to AC impedance and chronoamperometric measurements. In addition to the bands associated with adsorbed superoxide ions, broad spectral features assigned to the electrochemical polarization were also observed. These spectral features are believed to be due to polarization-induced changes in the optical properties of the electrode itself.

A state-of-the-art system for combustion CVD^[17] has been designed and constructed in our laboratory capable of producing nano-particles and nanostructured electrodes or interfaces of various materials. To date, nanostructured powders and coatings of many catalytically active materials have been successfully produced using the CCVD system. It is found that particle size and porosity can be readily controlled by adjusting deposition parameters, such as flame temperature, substrate temperature, fuel flow rate, and solution concentration. Our initial study focused on direct deposition of nanostructured electrodes for solid oxide fuel cells. Both cathode and anode were deposited by combustion CVD on a dense electrolyte. Further, combustion CVD is ideally suited for preparation of nano-sized powers for electrochemical and catalytic applications.

Combustion CVD System: A state-of-the-art Combustion CVD is explored as a technique for producing nano-powders and films of vastly different microstructures and morphologies suitable for applications as electrodes in electrochemical devices. Nano-sized powders of different oxide materials for fuel cells and batteries were produced by this novel technique. Several nano-structured films, porous or dense structures, columnar or honeycomb structures, are successfully prepared by carefully adjusting deposition

parameters. Furthermore, electrodes are deposited on doped-ceria electrolyte substrates for electrochemical measurements.

The performance of many electrochemical devices is often limited by losses at the electrode-electrolyte interface. In the case of fuel cells, the technology to produce thin electrolytes and new electrolyte materials is driving the anticipated operating temperature down, making the effect of the interfacial resistances on overall performance even more critical. Thus, one effective approach to dramatically improving the performance of solid-state electrochemical systems is to create novel electrodes or interfaces of minimal resistance (1, 2). While advances in new electrode materials are moving forward, approaches to create new electrode structures are also gaining ground as a method of decreasing cell losses (3). Nano-porous structures can provide extremely high surface areas, enhancing the rates of electrode reactions (4) but only if sufficient gas can be supplied.

Combustion chemical vapor deposition (Combustion CVD) is an economical approach to producing a wide range of thin films (5). In this process, a flammable solution containing precursor materials is atomized and sprayed through a specially designed nozzle together with fuel gas and then ignited to form a combustion flame. Chemical reactions to create the desired phases are accomplished within this high temperature flame. Thin films are formed when the flame is directed onto a substrate. This technique bears both economic and technical advantages over its counterparts. First, the process is performed in open-atmosphere, offering great flexibility of operation. The simple set-up and low initial capital investment are also attractive to many users. Technically, the deposition temperature can be adjusted in a very wide window, from less than 100°C to higher than 1500°C. Further, this technique is capable of depositing films with thickness between 10 nm and 30 μm at relatively high deposition rates.

Of importance to new research, is the flexibility of the Combustion CVD process. The process allows the deposition of composites, either from a single solution or through the use of multiple nozzles. In addition, since the precursors are supplied as dissolved metal ions, chemistry changes are achieved easily, allowing quick adjustment of dopants and stoichiometry of the final particles or films. Similarly, variations in structure and composition can be tailored through the thickness of the deposited films.

Schematically shown in Figure 7 is a state-of-the-art system for Combustion CVD, constructed in our laboratory, capable of producing nano-particles and nano-structured electrodes of various materials. The nanomizer (from Microcoating Technologies Inc.) is the key component of the system in creating nano-structured powders and films. To date, nano-structured powders and coatings of many catalytically active materials have been successfully produced using the Combustion CVD system.

Three types of porous electrodes for SOFCs are presented in this study. Shown in Figure 8(a) are cross-sectional and top view of a porous SSC+SDC film prepared by combustion CVD. The microstructure is similar to that prepared by conventional slurry coating or screen printing techniques where pores were formed uniformly between particles. In

Figure 8(b), cross section and top view of a columnar structure of SSC+SDC film deposited on a YSZ substrate is seen. The existence of larger vertical channels between columns would allow easier gas diffusion to the reaction interface. The columns themselves are composed of nano-particles, creating a highly active surface area for electrochemical reactions. The thickness of the porous electrode is about 30 to 40 μm , suitable for fuel cell application.

Shown in Figure 9 are some columnar structures with larger diffusion channels, which were prepared from the same solutions used for the SSC+SDC composite electrodes as those shown in Figure 8. More interestingly, with the same film material (SSC+SDC) was further fabricated in a radically different microstructure, a honeycomb structure as shown in Figure 10, with proper adjustment of deposition parameters.

CONCLUSIONS

Composites electrodes consisting of silver and bismuth vanadates exhibit remarkable catalytic activity for oxygen reduction at 500-550°C and greatly reduce the cathode-electrolyte (doped ceria) resistances of low temperature SOFCs, down to about 0.53 Ωcm^2 at 500°C and 0.21 Ωcm^2 at 550°C. The observed power densities of 231, 332, and 443 mWcm^{-2} at 500, 525 and 550°C, respectively, make it possible to operate SOFCs at temperatures about 500°C. While the long-term stability of the cathodes is yet to be characterized, the demonstrated remarkable performances (low interfacial resistances and high power densities) at low temperatures are very encouraging, implying that a new generation of low-temperature SOFCs is hopeful. Significant reduction in operating temperature will dramatically reduce not only the cost of materials but also the cost of fabrication. It also implies greater system reliability, longer operational life, and increased potential for mobile applications. Low-temperature SOFCs have great potential to be affordable for many applications, including residential and automotive applications.

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Figures

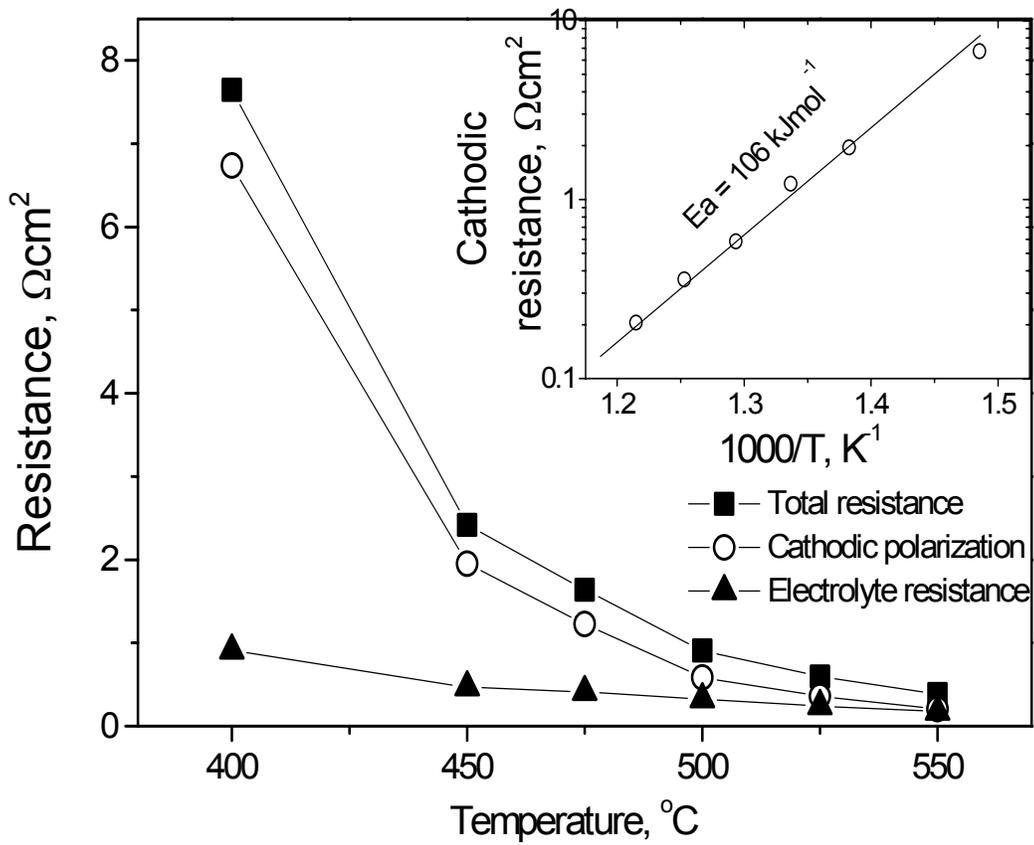


Figure 1. Total cell resistances, cathode-electrolyte interfacial resistances, and electrolyte resistances as determined from impedance spectra.

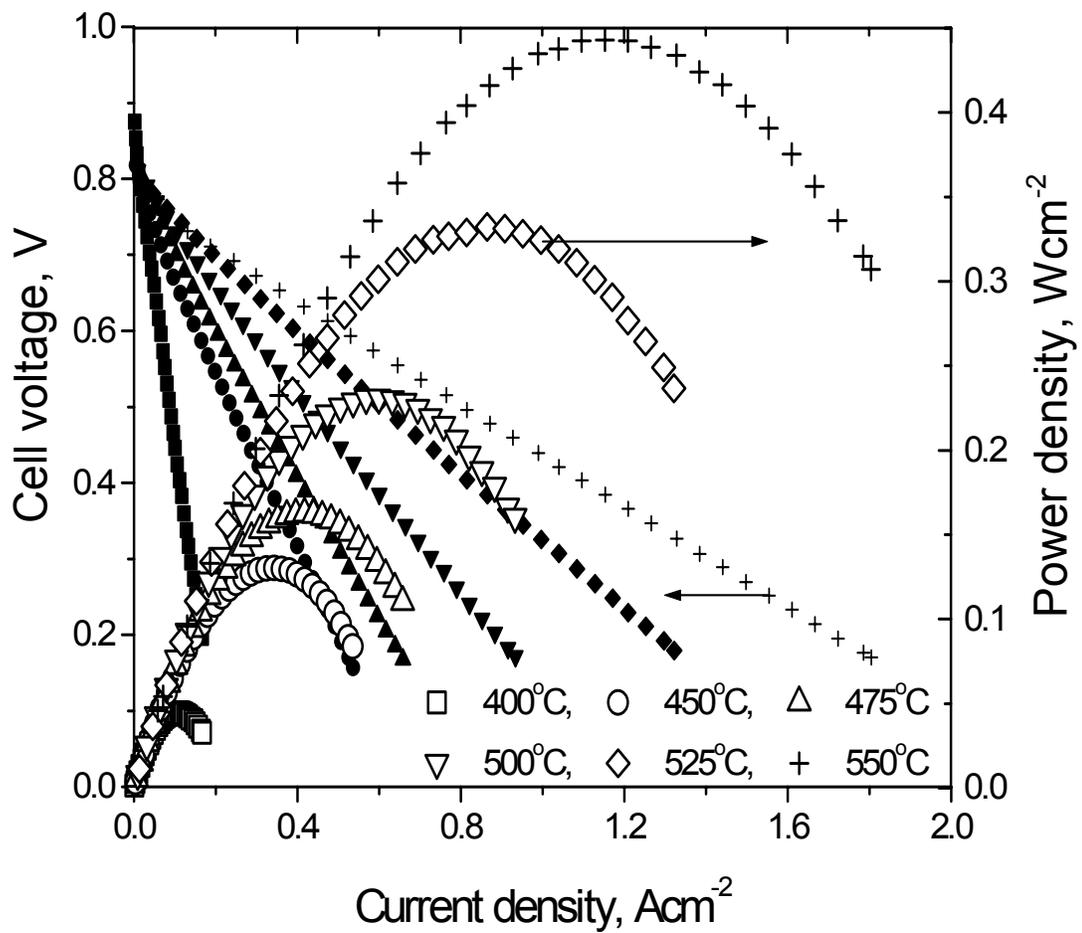


Figure 2. Cell voltages and power densities as a function of current densities for a fuel cell consisting of a Ag-BICUVOX composite cathode, a GDC electrolyte, and a Ni-GDC composite anode.

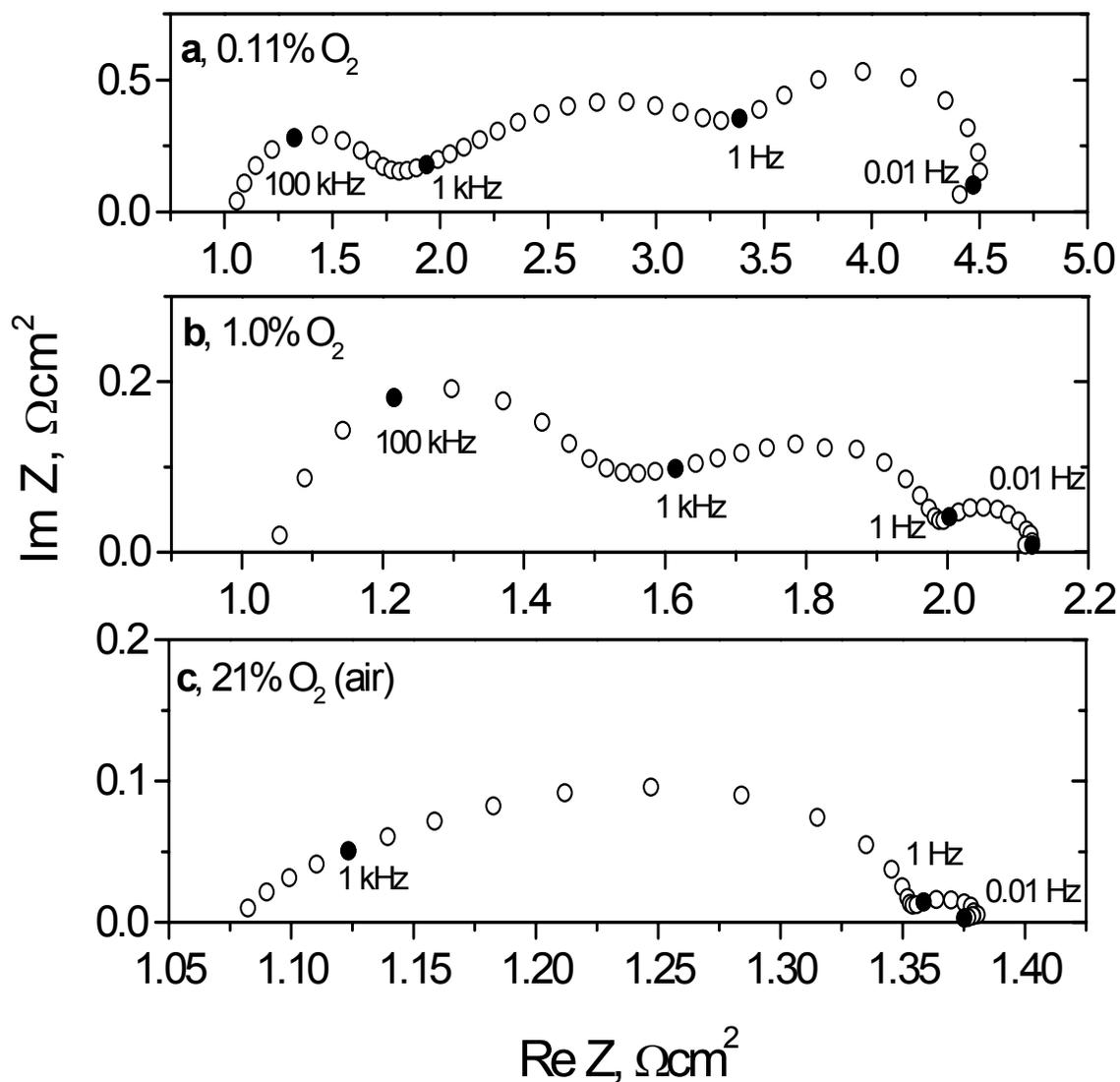


Figure 3. Impedance spectra of an YDB composite cathode measured at 600°C in gases containing different partial pressure of oxygen.

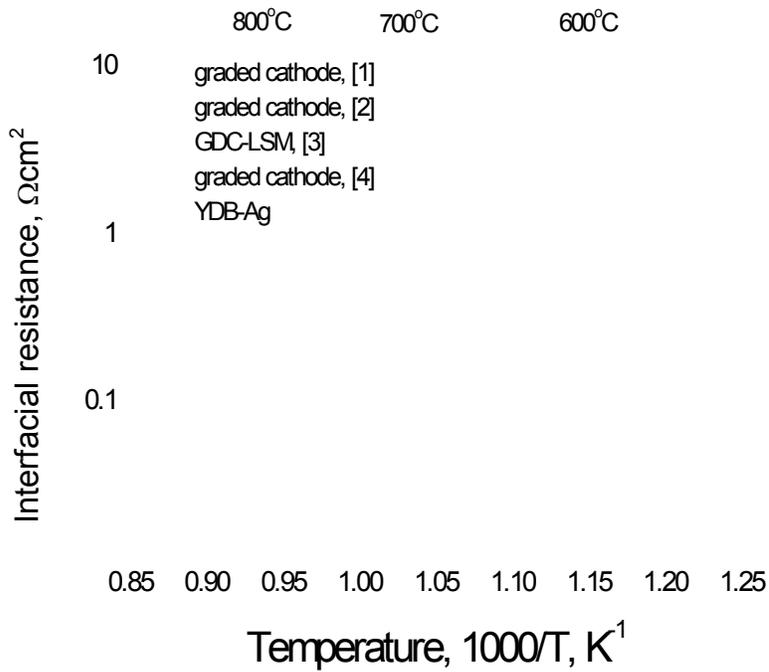


Figure 4. Interfacial polarization resistances of recently developed cathodes: Ag-YDB, a functional graded cathode, and an LSM-GDC composite.

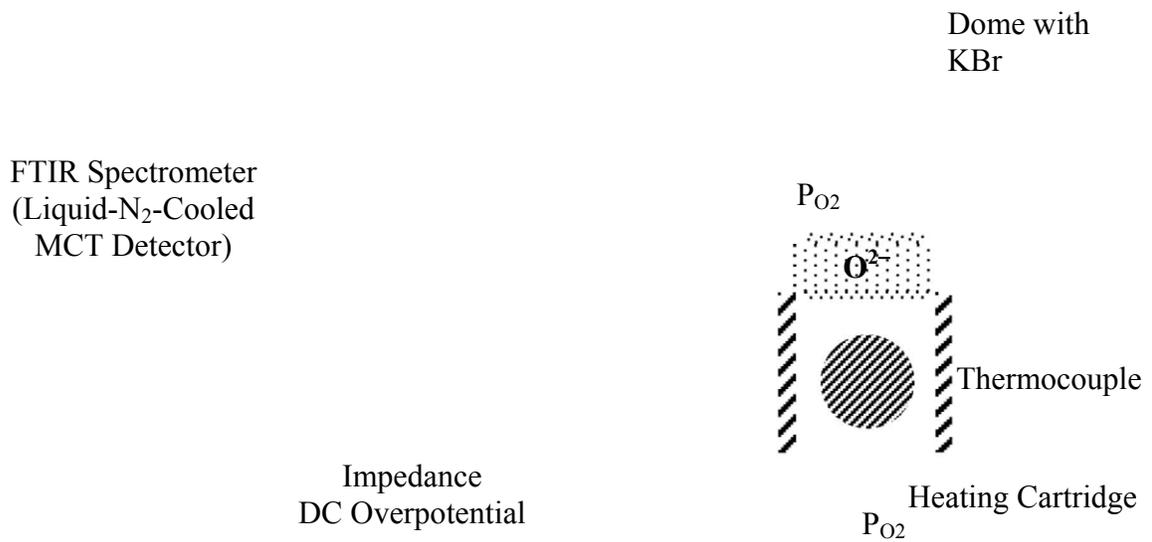


Figure 5. Schematic diagram of optical configuration for pd-FTIRES experiments.

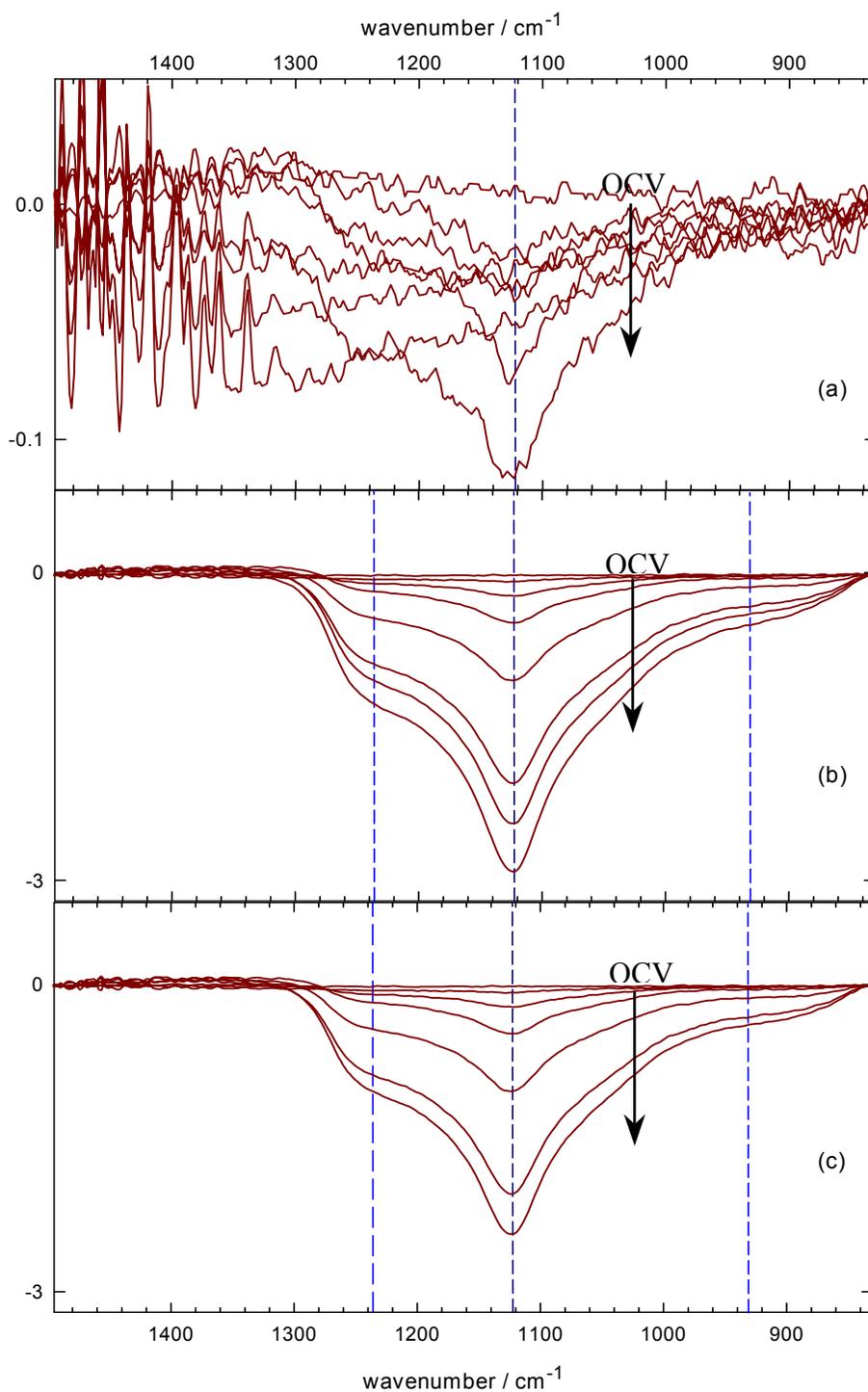


Figure 6 Comparison of pd-FTIRES spectra after local baseline correction for three different feed gas conditions: (a) air, (b) 1% O₂ in N₂ and (c) N₂. Cathodic overpotential excursions range from (a) 0 to 320 mV (b) 0 to 760 mV and (c) 0 to 690 mV. The arrows indicate the increasing direction of cathodic overpotentials.

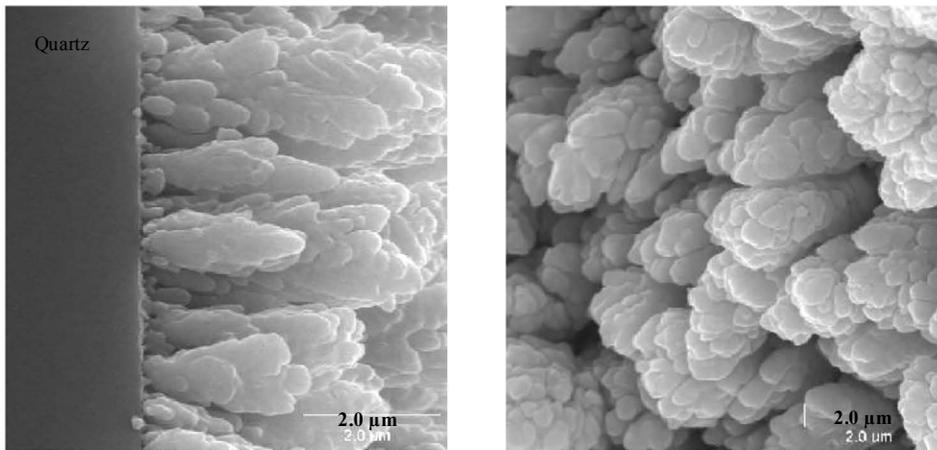


Figure 9. A more highly columnar structure of porous SSC-SDC composite electrode on a quartz substrate.

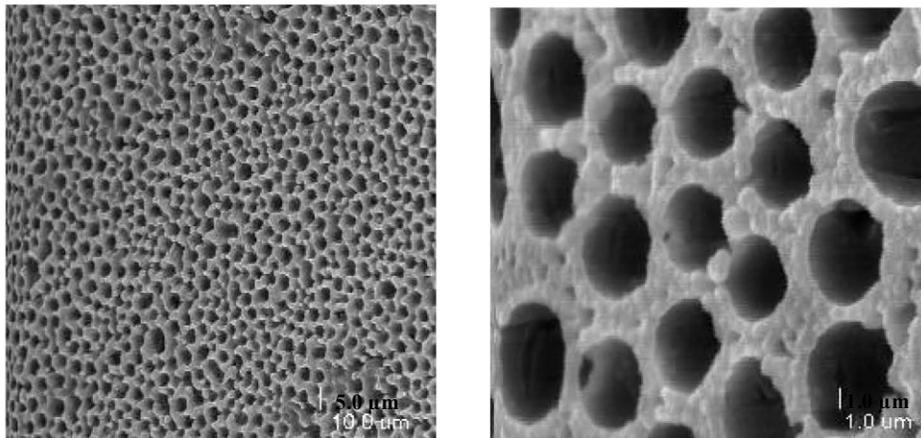


Figure 10. Unique honeycomb structure composed of SSC-SDC composite.

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