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**Potential cathode materials for application in proton ceramic fuel cells**

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## ABSTRACT

Based on quantum mechanical data obtained for the Y-doped BaZrO<sub>3</sub> electrolyte and Ni-anode Reactive Force Field parameters have been developed for further molecular dynamics simulations of the proton diffusion and electrode/electrolyte interfaces. Electronic and atomic structures of different terminations of the (001) BaZrO<sub>3</sub> surface have been studied using first-principles calculations. Several potential cathode materials for the Y-doped BaZrO<sub>3</sub> system were synthesized via glycine nitrate combustion method. Of the five potential cathode materials examined BaZr<sub>0.40</sub>Pr<sub>0.40</sub>Gd<sub>0.20</sub>O<sub>3</sub> and BaZr<sub>0.60</sub>Y<sub>0.20</sub>Co<sub>0.20</sub>O<sub>3</sub> appear to be the most promising for further applications in proton ceramic fuel cells. Fuel cell test of a Y-doped BaZrO<sub>3</sub> thin film using platinum ink for both electrodes have been performed. The obtained results shows that a robust method for fabricating crack-free thin membranes, as well as methods for sealing anode and cathode chambers, have successfully been developed.

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## INTRODUCTION

Many acceptor-doped perovskite-type oxides show high protonic conductivity at elevated temperatures. However, at present only electrolytes based on Y-doped BaZrO<sub>3</sub> (BYZ) combine high bulk proton conductivity with excellent chemical and mechanical stability. This allows one to consider BYZ as an attractive material for possible applications in a variety of electrochemical devices including proton ceramic fuel cells (PCFCs), hydrogen sensors for molten metals, H<sub>2</sub>/D<sub>2</sub> separators, and hydrogen pumps. The current limitation for application of BYZ in PCFCs is the extremely high grain boundary resistance, which leads to the relatively poor total conductivity. To understand the conduction process and the role of defects and dopants in transport at the molecular level, we are developing the multi-scale strategy based on accurate QM calculations of the relevant materials which are then used to derive a First Principles-based Reactive Force Field (ReaxFF) allowing large-scale MD simulations that enable the study of proton transport under realistic conditions as well as the role of grain boundaries, defects, dopants, etc. Follow-up experiments are used to validate the computational predictions and to formulate new problems and tasks. To date, we have carried out a series of quantum mechanical (QM) calculations on relevant metals (Pt, Zr, Y, Ba), metal alloys (Y/Zr, Y/Ba, and Zr/Ba), metal oxides (ZrO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, BaO, BaO<sub>2</sub>) and BYZ. Based on these data we started developing ReaxFF for further MD simulations of different physico-chemical processes in the electrolyte and at the electrode/electrolyte interface. As for the experimental part of the project, an initial screening of all transition elements in the series Sc to Zn has been carried out to find the best candidate for acceleration of the densification process of BaZrO<sub>3</sub> ceramics at lower temperature. It turned out that NiO, CuO and ZnO are the most effective additives for enhancing barium zirconate densification. Characterizations (X-ray diffraction, scanning electron microscopy, and impedance spectroscopy) of Zn-, Cu- and Ni-modified BYZ were performed to investigate properties of these materials.

In the forth semi-annual period we have focused on developing the ReaxFF for the BYZ electrolyte and Ni. The latter, as it was mentioned above, is an effective additive for the densification of the BYZ ceramics. Also, a Ni-BYZ cermet is successfully used as the anode material in a PCFC.

## EXECUTIVE SUMMARY

Based on first-principles QM data a ReaxFF have been developed and applied to model the proton diffusion in the BYZ electrolyte. A preliminary energy barrier for the proton diffusion obtained from a restrained ReaxFF molecular dynamics simulation of the above-mentioned process in BYZ is about 0.7 eV, which is close enough to the experimental value of 0.44 eV. A series of QM calculations have been carried out on Ni-surfaces and Ni-clusters. The results of these calculations were then used for developing the initial ReaxFF potentials for Ni. At current stage the ReaxFF can describe H- and O-binding to both Ni-surfaces and Ni-clusters and reproduce the QM data. Electronic and atomic structures of BaO and ZrO<sub>2</sub> terminations of the (001) BaZrO<sub>3</sub> surface have been studied for further modeling of the electrode/electrolyte interfaces and the grain boundary properties. The surface energies at both terminations are very close, 1.064 and 1.032 J/m<sup>2</sup>. Several potential cathode materials for the Y-doped BaZrO<sub>3</sub> system have been synthesized and characterized. Of the five potential cathode materials examined BaZr<sub>0.40</sub>Pr<sub>0.40</sub>Gd<sub>0.20</sub>O<sub>3</sub> and BaZr<sub>0.60</sub>Y<sub>0.20</sub>Co<sub>0.20</sub>O<sub>3</sub> appear to be the most promising for further applications in proton ceramic

fuel cells. However, the possibility that better materials exist has hardly been ruled and additional screening continues. Fabrication of cathode-supported cells is also under development.

Fuel cell test of a BYZ thin film using platinum ink for both electrodes have been performed. This test showed that a robust method for fabricating crack-free thin membranes, as well as methods for sealing anode and cathode chambers, were successfully developed.

## RESULTS AND DISCUSSION

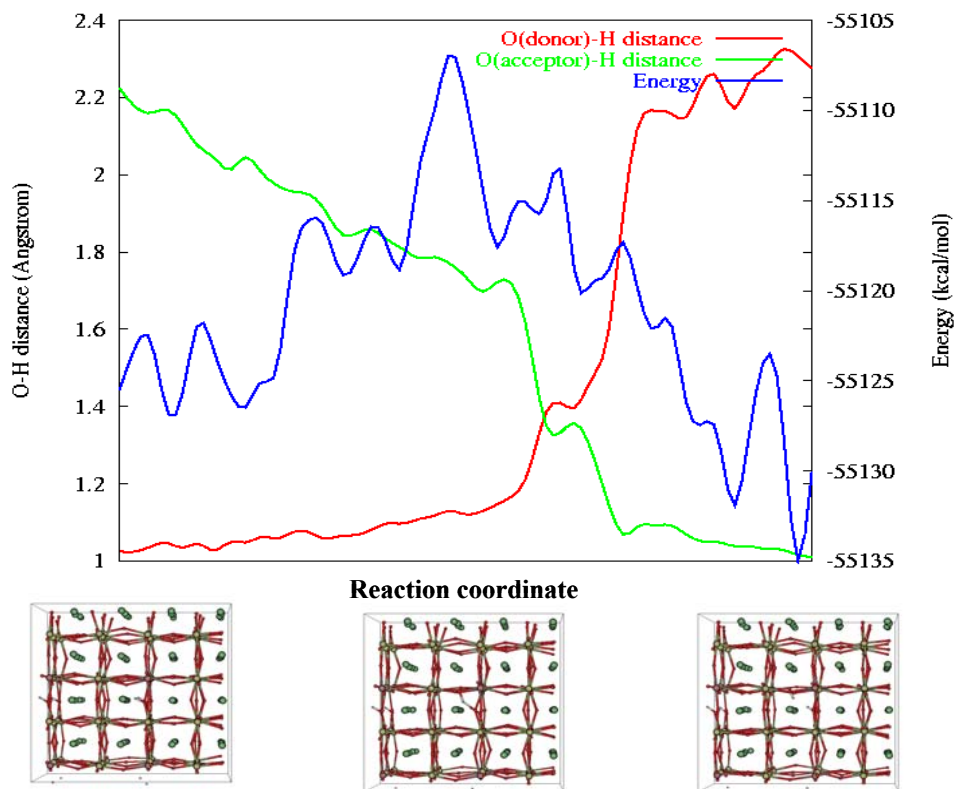
### *THEORETICAL*

The ReaxFF [1, 2] is especially designed to describe chemical reactivity, dissociation and formation of chemical bonds, surfaces, defects, diffusion, etc. It is completely based on *ab initio* QM calculations. QM calculations have been carried out using the pseudo-potential local basis set code “SeqQuest” [3] for periodic structures and the *ab initio* electronic structure package “Jaguar” [4] for cluster calculations. The obtained QM data were then used to optimize ReaxFF parameters. In the ReaxFF parameter optimization most weight was given to the low-energy phases. For the high-energy phases we gave little weight but rather focused on making sure that the ReaxFF gets the correct energy with respect to the low-energy phases. The most important key features of the ReaxFF are following:

- The ReaxFF employs a bond length/bond order relationship to get a smooth transition from non-bonded to single, double and triple bonded systems. Bond orders are updated every iteration.
- Non-bonded interactions (van der Waals, Coulomb) are calculated between every atom pair, irrespective of connectivity. Excessive close-range nonbonded interactions are avoided by shielding.
- All connectivity-dependent interactions (i.e. valence and torsion angles) are made bond-order dependent, ensuring that their energy contributions disappear upon bond dissociation.
- The ReaxFF uses a geometry-dependent charge calculation scheme that accounts for polarization effects.
- No discontinuities are in energy or forces even during reactions.
- Users do not have to pre-define reactive sites or reaction pathways; potential functions should be able to automatically handle coordination changes associated with reactions.
- Each element is represented by only one atom type in the force field; the ReaxFF should be able to determine equilibrium bond lengths, valence angles, etc. from chemical environment.

In our previous work on developing the initial ReaxFF potentials for BYZ we paid attention to reproduce the QM relative energies and geometries for various structural configurations of BYZ in which the hydrogen atoms occupied various possible positions and we obtained good agreement between the QM and ReaxFF data. At the current stage of the ReaxFF development we have focused on the proton diffusion in BYZ. Fig.1 shows the ReaxFF energy obtained from a restrained molecular dynamics (MD) simulation of the proton diffusion through the BYZ lattice at T=100K. The energy barrier for this process is about 0.7 eV (~15 kcal/mol), which is not too far from the experimental value of the activation energy of 0.44 eV [5]. It should be noted that we continue

developing the ReaxFF potentials for BYZ and expect further improvements in description of the proton diffusion in BYZ.

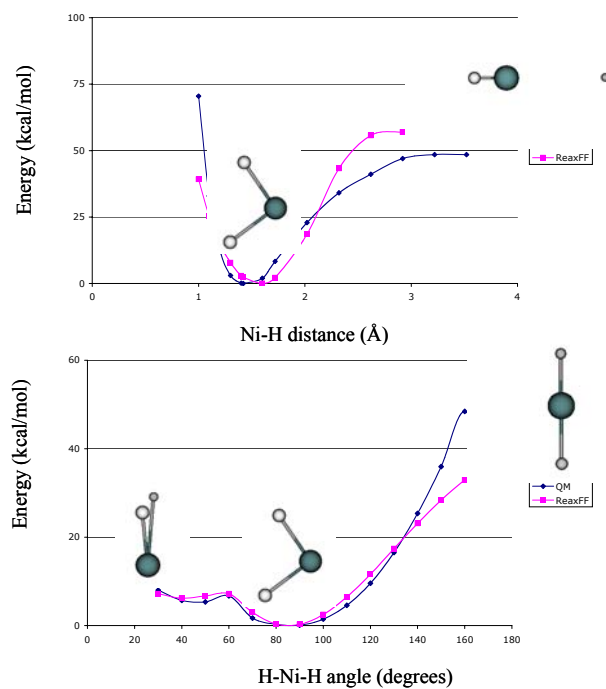


**Figure1.** ReaxFF MD simulation of the proton diffusion through the BYZ lattice at T=100K.

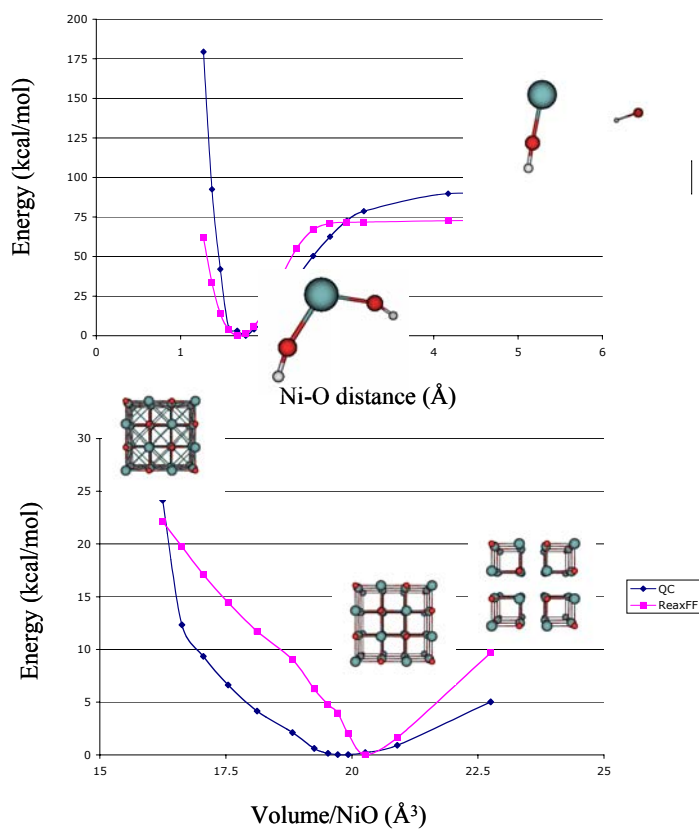
In fuel cells electrolytes are in contact with catalysts and electrodes forming membrane-electrode assemblies (MEAs). The electrolyte-electrodes interfaces are the primary source for power loss at small currents. Therefore, it is very important to develop computational tools for modeling interfaces. We started this work from the anode side. The primary function of the anode in a PCFC is to facilitate the half cell reaction,  $\frac{1}{2} \text{H}_2 \rightarrow \text{H}^+$  and  $\text{e}^-$  [assuming  $\text{H}_2$  as the fuel]. If a hydrocarbon fuel is utilized, the anode must also catalyze the reformation of the fuel (which is mixed with  $\text{H}_2\text{O}$ ) to produce  $\text{CO}_2$  and  $\text{H}_2$ . Ni has been particularly successful as the anode material for conventional solid oxide fuel cells (SOFCs). We have carried out a series of QM calculations on Ni, the results of which are used for the development of the initial ReaxFF potentials. Figures 2-4 show examples of this work. From these Figures one can see that the ReaxFF can describe H- and O-binding to both Ni-surfaces and Ni-clusters and reproduce the QM data. To complete the ReaxFF parameterization we need more Ni cases, including QM calculations on various periodic structures. This work is in progress.

To model BYZ/electrode interfaces and grain boundaries we need a reliable ReaxFF description of the oxide surfaces based on relevant QM data. We started QM calculations on  $\text{BaZrO}_3$  surfaces using the SeqQuest code. Electronic and atomic structures of different terminations of the (001) non-polar orientation of  $\text{BaZrO}_3$  surface have been studied. We found that the surface is “weakly

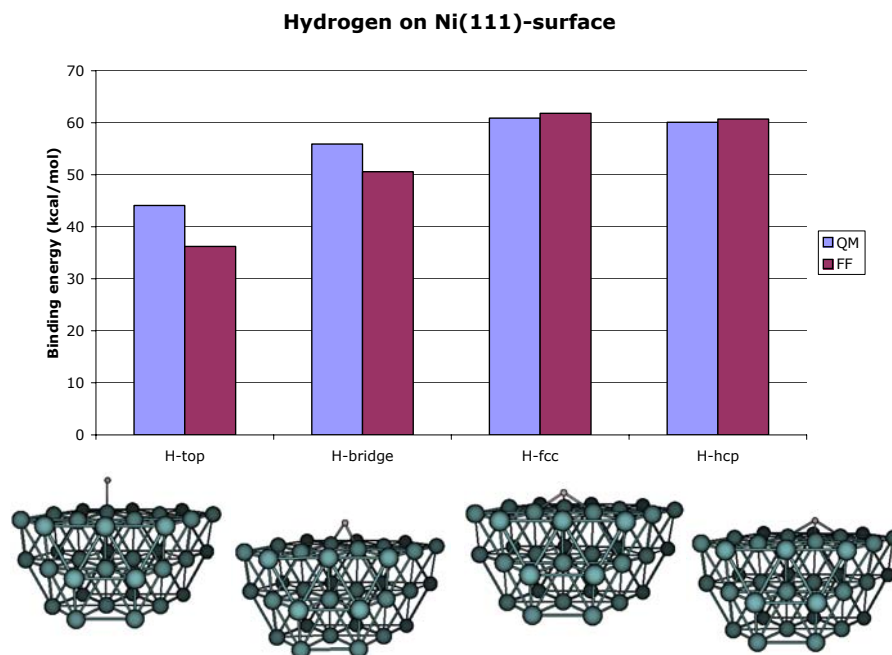




**Figure2.** Ni-H bond dissociation and H-Ni-H angle bending in  $\text{NiH}_2$ .



**Figure3.** Ni-O bond dissociation in  $\text{Ni(OH)}_2$  and  $\text{NiO}$  equation of states.



**Figure 4.** Hydrogen on the Ni(111)-surface.

polar”. The surface polarity is compensated by a small charge, about a quarter of an electron, localized at the surface layer. The surface energies at both, BaO and ZrO<sub>2</sub>, terminations are very close (see Table 1).

**Table 1.** The relaxed surface energies for slabs of 9-layer thickness, in eV/unit cell and J/m<sup>2</sup>. Cleavage energy values are also included, in eV/unit cell and J/m<sup>2</sup>.

Termination	Relaxed Surface Energy (eV/unit cell)	Relaxed Surface Energy (J/m <sup>2</sup> )	Cleavage Energy (eV/unit cell)	Cleavage Energy (J/m <sup>2</sup> )
BaO (001)	1.197	1.064	1.316	1.170
ZrO <sub>2</sub> (001)	1.161	1.032	1.316	1.170

We also found that the (001)-BaO and (001)-ZrO<sub>2</sub> terminated surfaces have bandgap values smaller than that of the bulk crystal (see Table 2).

**Table 2.** Calculated bandgap values for the BaO and ZrO<sub>2</sub> (001) surface terminations.

Termination	Layers	Bandgap (eV)
BaO (001)	9	3.036
ZrO <sub>2</sub> (001)	9	2.396
Bulk	9	3.102

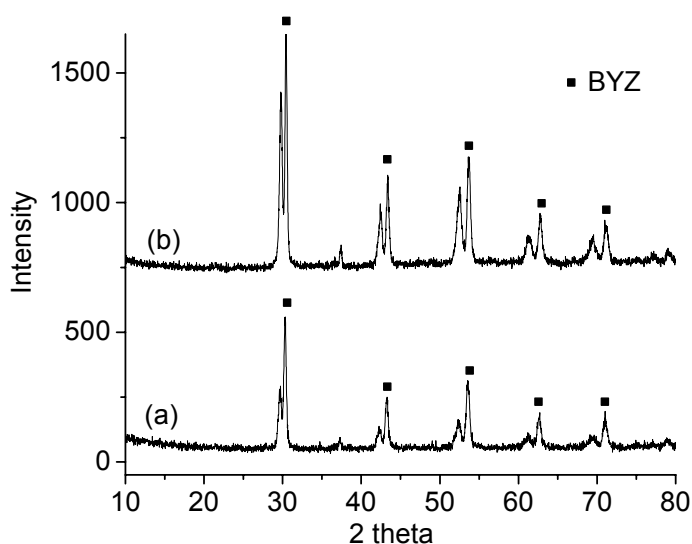
Further BaZrO<sub>3</sub> and BYZ surface investigations, including other surface orientations, are needed to better understand the surface properties and structures.

## EXPERIMENTAL

### Screening of potential cathode materials (transition metal perovskites)

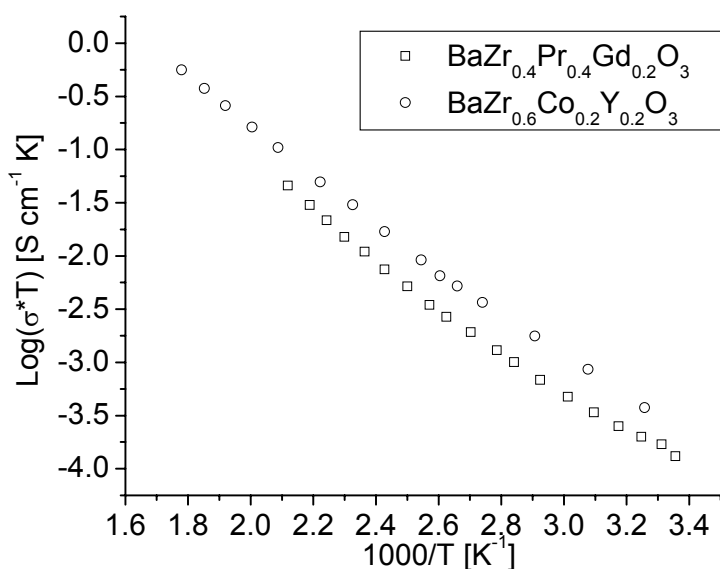
Several potential cathode materials for the doped barium zirconate system were synthesized via the glycine nitrate combustion method. The appropriate metal-nitrates and a glycine to nitrate ratio of 1:2 was utilized. The following cathodes were synthesized: BaZr<sub>0.40</sub>Pr<sub>0.40</sub>Gd<sub>0.20</sub>O<sub>3</sub>, BaZr<sub>0.70</sub>Pr<sub>0.10</sub>Gd<sub>0.20</sub>O<sub>3</sub>, BaZr<sub>0.80</sub>Co<sub>0.20</sub>O<sub>3</sub>, BaZr<sub>0.60</sub>Y<sub>0.20</sub>Co<sub>0.20</sub>O<sub>3</sub> and BaPr<sub>0.85</sub>Y<sub>0.15</sub>O<sub>3</sub>. All formed single phase perovskites as determined by X-ray power diffraction (data not shown). The Pr rich compound, BaPr<sub>0.85</sub>Y<sub>0.15</sub>O<sub>3</sub>, however, proved to be unstable with time and at high temperature and was not considered further.

Potential cathodes were mixed with BaZr<sub>0.85</sub>Y<sub>0.15</sub>O<sub>3</sub> (BYZ) and calcined at 700°C (maximum fuel cell operating temperature) for 24 hours to observe the possibility of a reaction/interdiffusion. Under these conditions, BaZr<sub>0.70</sub>Pr<sub>0.10</sub>Gd<sub>0.20</sub>O<sub>3</sub> and BaZr<sub>0.80</sub>Co<sub>0.20</sub>O<sub>3</sub> completely reacted with BYZ to yield a single, solid-solution perovskite phase and were not considered further. In contrast, mixtures of BaZr<sub>0.40</sub>Pr<sub>0.40</sub>Gd<sub>0.20</sub>O<sub>3</sub> with BYZ and of BaZr<sub>0.60</sub>Y<sub>0.20</sub>Co<sub>0.20</sub>O<sub>3</sub> with BYZ retained two perovskite phases, Figure 5, although the possibility of slight interdiffusion cannot be entirely ruled out.



**Figure 5.** Diffraction patterns obtained from mixtures of (a) BYZ + BaZr<sub>0.60</sub>Y<sub>0.20</sub>Co<sub>0.20</sub>O<sub>3</sub> and (b) BYZ + BaZr<sub>0.40</sub>Pr<sub>0.40</sub>Gd<sub>0.20</sub>O<sub>3</sub>, after exposure to 700°C for 24 hrs showing that two separate perovskite phases are retained.

The bulk conductivity of BaZr<sub>0.40</sub>Pr<sub>0.40</sub>Gd<sub>0.20</sub>O<sub>3</sub> and BaZr<sub>0.60</sub>Y<sub>0.20</sub>Co<sub>0.20</sub>O<sub>3</sub> was measured by AC impedance methods in a wet air atmosphere, and is shown in Figure 6. Both materials are promising because they have conductivity comparable to that of BYZ in the temperature range of



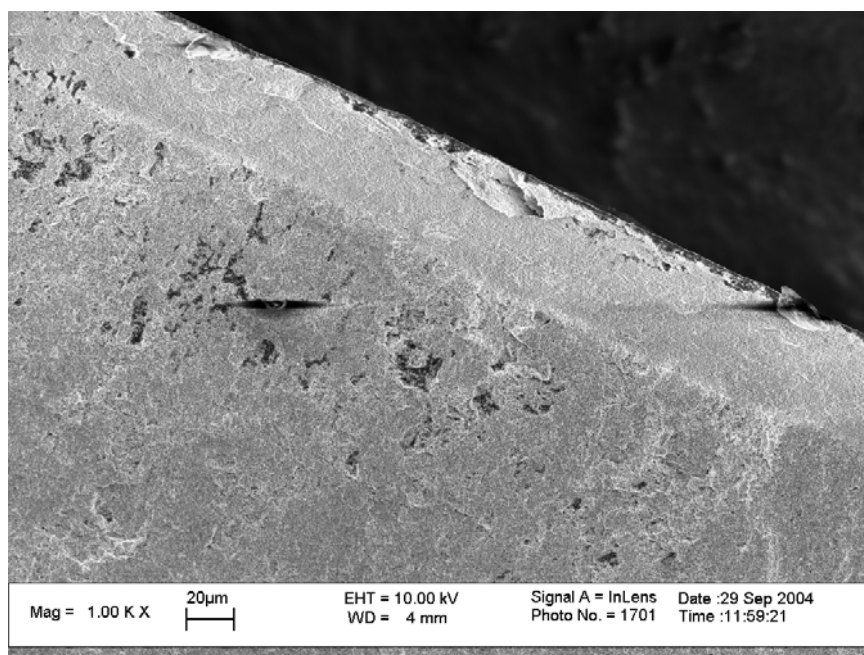
**Figure 6.** Bulk conductivity of two potential cathode materials as measured in wet air atmosphere.

interest. Surprisingly the activation energy of  $\text{BaZr}_{0.40}\text{Pr}_{0.40}\text{Gd}_{0.20}\text{O}_3$  was measured as 0.40eV and  $\text{BaZr}_{0.60}\text{Y}_{0.20}\text{Co}_{0.20}\text{O}_3$  as 0.42eV, which are close to 0.44eV of BYZ bulk conductivity. It was expected that the addition of transition metals would lead to an increase in electronic conductivity that should result in lower activation energies.

### Development of cathode and electrolyte deposition methods

Two cathode deposition techniques, both based on colloidal methods, were pursued for the fabrication of electrolyte-supported (and ultimately anode-supported) fuel cells using the two potential cathode materials,  $\text{BaZr}_{0.40}\text{Pr}_{0.40}\text{Gd}_{0.20}\text{O}_3$  and  $\text{BaZr}_{0.60}\text{Y}_{0.20}\text{Co}_{0.20}\text{O}_3$ . In the first method, the colloidal solution was deposited onto BYZ by mechanical methods using a simple paintbrush. After calcination at 900°C for 2 hours, the cathode adhesion to the electrolyte was found to be poor and the cathode could be easily removed. Accordingly, the method was abandoned. In the second method, the colloidal solution was deposited by spraying. Better contact between the cathode and the electrolyte was achieved, particularly in the case of  $\text{BaZr}_{0.60}\text{Y}_{0.20}\text{Co}_{0.20}\text{O}_3$ , justifying the greater effort involved in this method. In the case of  $\text{BaZr}_{0.40}\text{Pr}_{0.40}\text{Gd}_{0.20}\text{O}_3$ , although the contact was improved by spray deposition, the cathode eventually detached over time. It is believed that the introduction of a porous BYZ layer between the electrolyte and cathode will further improve the adhesion.

Fabrication of cathode-supported cells is also under development. Such structures would be implemented should the cathode overpotential be lower than that of the anode. Our development of highly sinterable BYZ via the introduction of 4 mole % Zn (BYZ-Zn4) has made it possible to pursue cathode supported fuel cells. Fabrication methods to date have involved dual pressing, in which a thick cathode layer is uniaxially pressed and a thin electrolyte layer deposited atop this layer and the two layers pressed together (again, uniaxially). Sintering is carried out at 1300-1400°C, at which BYZ-Zn4 densification is greatest. Figure 7 shows a BYZ-Zn4 electrolyte on a



**Figure 7.** Micrograph of a cathode-supported thin-film cell, 20  $\mu\text{m}$  BYZ supported on  $\text{BaZr}_{0.40}\text{Pr}_{0.40}\text{Gd}_{0.20}\text{O}_3$ .

$\text{BaZr}_{0.40}\text{Pr}_{0.40}\text{Gd}_{0.20}\text{O}_3$  cathode support. The electrolyte is approximately 40-50 micrometers thick, however it is not yet fully densified. Further optimization of the co-sintering temperature is needed to develop a thin dense electrolyte on a cathode supported MEA.

Of the five potential cathode materials examined  $\text{BaZr}_{0.40}\text{Pr}_{0.40}\text{Gd}_{0.20}\text{O}_3$  and  $\text{BaZr}_{0.60}\text{Y}_{0.20}\text{Co}_{0.20}\text{O}_3$  appear the most promising. However, the possibility that better materials exist has hardly been ruled and additional screening continues.

### Testing of thin-membrane fuel cells with the baseline (Pt) cathode

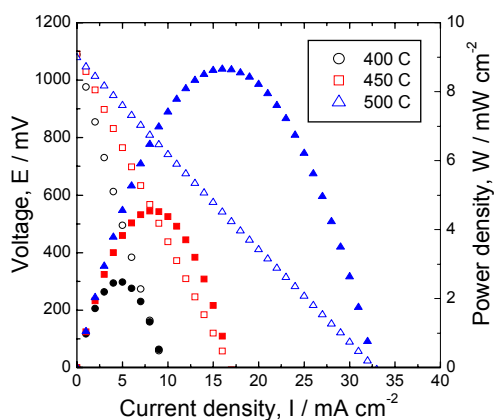
Figure 8 is a result of fuel cell test of BYZ thin film (100  $\mu\text{m}$ ) using platinum ink for both electrodes, operated with humidified hydrogen and humidified oxygen supplied to the anode and cathode, respectively. As evident from the figure, power generation was clearly confirmed. Open circuit voltage (OCV), short circuit current density and peak power densities were as follows (Table 3).

**Table 3.** Short circuit current density and peak power densities

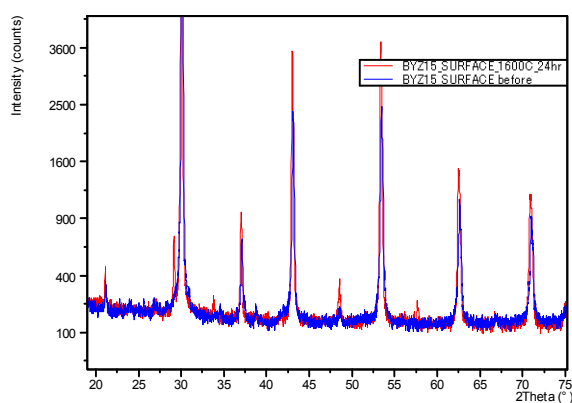
	OCV (mV)	Short circuit current ( $\text{mA}/\text{cm}^2$ )	Peak power density ( $\text{mW}/\text{cm}^2$ )
400°C	1089	10	3
450°C	1091	17	5
500°C	1079	33	9

\* 50cc  $\text{H}_2$  and  $\text{O}_2$  humidified 50 °C water.

Despite the relatively thin membrane (100  $\mu\text{m}$ ), the measured OCVs are very close to the theoretical values (1.15 V at 400°C and 1.13 V at 500°C). Thus, we have successfully developed a robust method for fabricating crack-free thin-membranes, as well as methods for sealing anode and cathode chambers. However, the short circuit current and peak power densities are not in the range expected from the conductivity of BYZ (presented in earlier reports). That is, the resistance of the cell is higher than expected. The highly linear dependence of voltage on current density strongly suggests that the potential drop is not due to electrode behavior but rather the electrolyte itself. X-ray powder diffraction patterns of the surface of the membrane before and after sintering (24 hr at 1600°C) are compared in Figure 9. It is apparent that a fluorite phase is formed upon sintering. This phase is certainly the by-product of BaO evaporation during the high temperature sintering and may be source of high resistance of the electrolyte. Our thin film fabrication methods will be integrated with our highly sinterable barium zirconate, BYZ-Zn<sub>4</sub>, to yield high power density fuel cells.



**Figure 8.** I-V curve of 100  $\mu\text{m}$  BYZ electrolyte for hydrogen fuel cell. Painted platinum was used as electrocatalyst for anode and cathode.



**Figure 9.** XRD pattern of BYZ thin file before sintering and after sintering (24 hr at 1600°C)

## CONCLUSIONS

Initial ReaxFF potentials have been developed and applied to model the proton diffusion in the BYZ electrolyte. A preliminary energy barrier for the proton diffusion in BYZ obtained from a restrained ReaxFF molecular dynamics simulation is about 0.7 eV which is close enough to the experimental value of 0.44 eV.

A series of QM calculations have been carried out on Ni-surfaces and Ni-clusters. The results of these calculations were then used for developing ReaxFF potentials for Ni.

The ReaxFF developed for Ni can describe H- and O-binding to both Ni-surfaces and Ni-clusters and reproduce the QM data.

Electronic and atomic structures of BaO and ZrO<sub>2</sub> terminations of the (001) BaZrO<sub>3</sub> surface have been studied. The surface energies at both terminations are very close, 1.064 and 1.032 J/m<sup>2</sup>, and the bandgap values smaller than that of the BaZrO<sub>3</sub> bulk crystal.

Several potential cathode materials for the Y-doped BaZrO<sub>3</sub> system have been synthesized and characterized. Of the five potential cathode materials examined BaZr<sub>0.40</sub>Pr<sub>0.40</sub>Gd<sub>0.20</sub>O<sub>3</sub> and BaZr<sub>0.60</sub>Y<sub>0.20</sub>Co<sub>0.20</sub>O<sub>3</sub> appear to be the most promising for further applications in proton ceramic fuel cells.

Two cathode deposition techniques based on colloidal methods were pursued for the fabrication of electrolyte-supported fuel cells. The method, in which the colloidal solution was deposited by spraying, provides better contact between the cathode and the BYZ electrolyte.

Fabrication of cathode-supported cells is also under development. Further optimization of the co-sintering temperature is needed to develop a thin dense electrolyte on a cathode supported MEA.

Fuel cell test of BYZ thin film using platinum ink for both electrodes have been performed. The measured OCVs are very closed to the theoretical values, 1.15 V at 400°C and 1.13 V at 500°C. The obtained results shows that we have successfully developed a robust method for fabricating crack-free thin membranes, as well as methods for sealing anode and cathode chambers.

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## LIST OF ACRONYMS AND ABBREVIATIONS

BYZ -  $\text{BaZr}_{1-x}\text{Y}_x\text{O}_{3-\delta}$

MD - Molecular Dynamics,

MEA – Membrane-Electrode Assembly

OCV – Open Circuit Voltage

PCFC – Proton Ceramic Fuel Cell,

QM - Quantum Mechanics,

ReaxFF - First Principles-Based Reactive Force Field,

SOFC –Solid Oxide Fuel Cell

XRD – X-ray Diffraction