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Potential electrode materials for application in proton ceramic fuel cells.

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ABSTRACT

A series of Quantum Mechanical (QM) calculations on Y-doped $BaZrO_3$ (BYZ) periodic structures have been performed and calculated energy barriers for the intra-octahedra and inter-octahedra proton transfer have been found. The inter-octahedra proton transfer dominates in the BYZ electrolyte. Several potential cathode materials for the Y-doped $BaZrO_3$ system were synthesized via glycine nitrate combustion method. Of the five potential cathode materials examined $BaZr_{0.40}Pr_{0.40}Gd_{0.20}O_3$ and $BaZr_{0.60}Y_{0.20}Co_{0.20}O_3$ appear to be the most promising for further applications in proton ceramic fuel cells (PCFCs). Potential anode electrocatalysts (metals) have been screened for reactivity with $BaZr_{1-x}Y_xO_{3-\delta}$, fabrication compatibility, and chemical stability in fuel cell environment.

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INTRODUCTION

In most proton conductors the principal features of the proton transport mechanism can be described as a two-step process, 1) fast rotational diffusion of a complex ion that includes a proton, for instance, a [BO_6H]-octahedron in perovskites, and 2) proton transfer within a hydrogen bond between two neighboring complex ions. Both experimental and theoretical results show that the rotational diffusion occurs with a low activation barrier and that the proton transfer is a rate-limiting step in the proton transport mechanism. However, this two-step process only generally describes the proton diffusion remaining details of this process out of frame. Experimentally, it is difficult to determine proton migration pathways and energy barriers along them. First-principles calculations, such as DFT-based methods, can be informative enough for examining the atomic-scale proton movement. Proton defects can be modeled and calculated in a supercell that is multiples of the unit cell for the undefected structure and then energy barriers for possible proton migration pathways can be calculated. The calculations have been performed using DFT theory in the Generalized Gradient Approximation (GGA), which yields excellent structural energetics for many oxides. We used SEQQUEST [1] a Gaussian-based linear combination of atomic orbitals method jointly being developed between Sandia National Laboratories (Dr. Peter Schultz) and Caltech. Pseudopotentials were used to replace the core electrons. All calculations were performed at $T = 0$ K.

EXECUTIVE SUMMARY

A series of QM calculations on BYZ periodic structures have been performed and energy barriers for the intra-octahedra and inter-octahedra proton transfer have been calculated. The activation energy for the intra-octahedron proton transfer is found to be equal to 0.55 eV, while that for the inter-octahedra proton transfer is 0.44 eV, which is in perfect agreement with the experimental value, 0.44 eV. Most probably, the inter-octahedra proton transfer is observed in the BYZ electrolyte.

Several potential cathode materials for the Y-doped $BaZrO_3$ system have been synthesized and characterized. Of the five potential cathode materials examined $BaZr_{0.40}Pr_{0.40}Gd_{0.20}O_3$ and $BaZr_{0.60}Y_{0.20}Co_{0.20}O_3$ appear to be the most promising for further applications in proton ceramic fuel cells. Processing of the samples needs to be to suppress Ba loss during the sintering. Further screening of cathode materials continues.

Potential anode electrocatalysts (metals) have been screened for reactivity with $BaZr_{1-x}Y_xO_{3-\delta}$, fabrication compatibility, and chemical stability in fuel cell environment. It was found that NiO easily diffuse into the BYZ layer during sintering. Bi-layer and tri-layer BYZ systems with varying porosity have been developed. The support is a porous BYZ layer while the electrolyte is a fully densified layer.

RESULTS AND DISCUSSION

THEORETICAL

Energy barriers for proton diffusion

In our previous work on developing ReaxFF potentials for BYZ we trained the ReaxFF 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. We also found that the energy barrier for the proton diffusion in BYZ is about 0.8 eV, while the experimental value for the activation energy was 0.44 eV [2]. It is expected that the energy barrier for proton transfer significantly contributes to the activation energy. It should be noted that the value of 0.83 eV was obtained for the calculated activation energy for the proton diffusion in BYZ using the quantum molecular dynamics approach [3]. The conclusion made in this work was following: only intra-octahedra proton transfers on edges of the distorted BO_6-octahedra are observed in the BYZ electrolyte. However, the noticeable difference in the values for the calculated and experimental activation energies for the proton diffusion in BYZ required further computational work to better describe the proton diffusion energetics in BYZ. Thus, we have carried out a series of QM calculations on BYZ periodic structures to find pathways and energy barriers for the proton diffusion. We started off by investigating the energy barrier for the intra-octahedron proton transfer on the edge of the distorted ZrO_6-octahedron (see Fig.1).

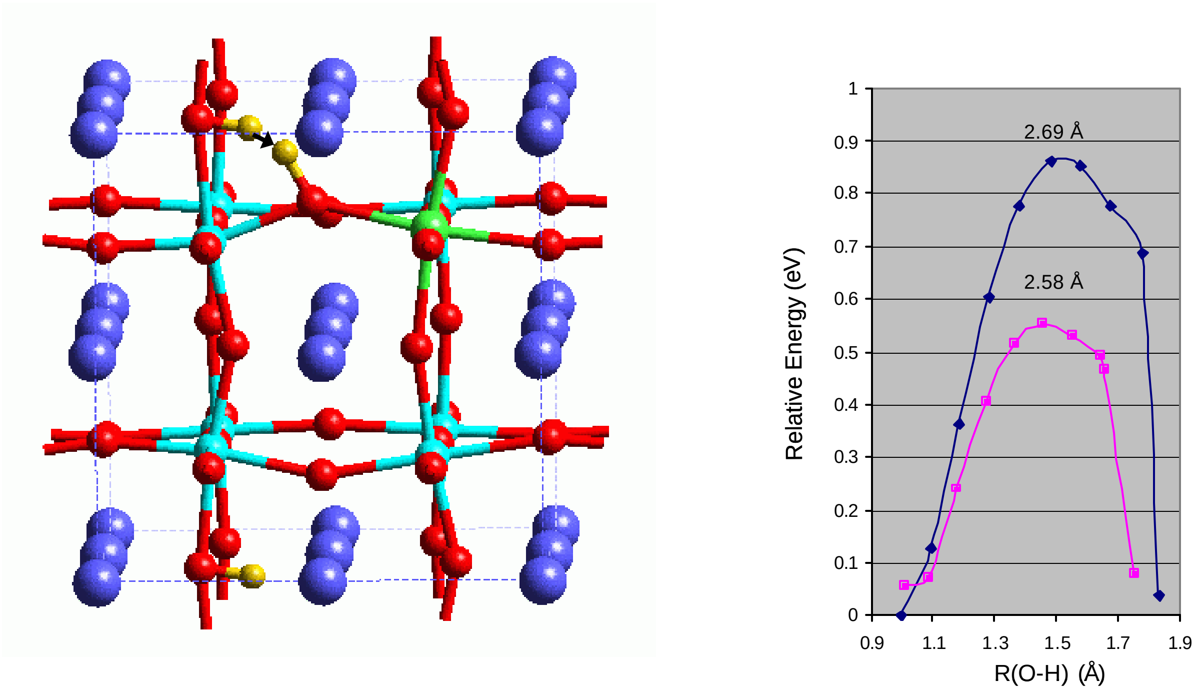

Figure 1. Intra-octahedron proton transfer in BYZ.
Left – BYZ structure (Ba - dark blue, Zr- blue, Y- green, O - red , and H - yellow balls, respectively);
right – energy barrier for intra-octahedron proton transfer.

It turned out that the barrier significantly depends on the length of the O – O edge of the ZrO_6 octahedron. In the BYZ optimized structure, in which all atoms were relaxed, the length of the O – O edge is 2.69 Å and the calculated energy barrier for the proton transfer is 0.86 eV. Then we decreased the length of the O – O edge down to 2.58 Å, fixed two corresponding oxygen atoms, and relaxed all remaining atoms. The energy of the BYZ structure optimized by such a way increased by 0.06 eV because of the further distortion of the ZrO_6-octahedron, while the energy barrier for the proton transfer dropped to 0.50 eV. Therefore, the activation energy for the intra-octahedron proton transfer is approximately 0.55 eV.

Another possible proton pathway lies outside of the BO_6 octahedra and hydrogen bonding occurs between oxygen atoms of the neighboring BO_6 octahedra. In this case, the proton transfer is inter-octahedra (see Fig.2).

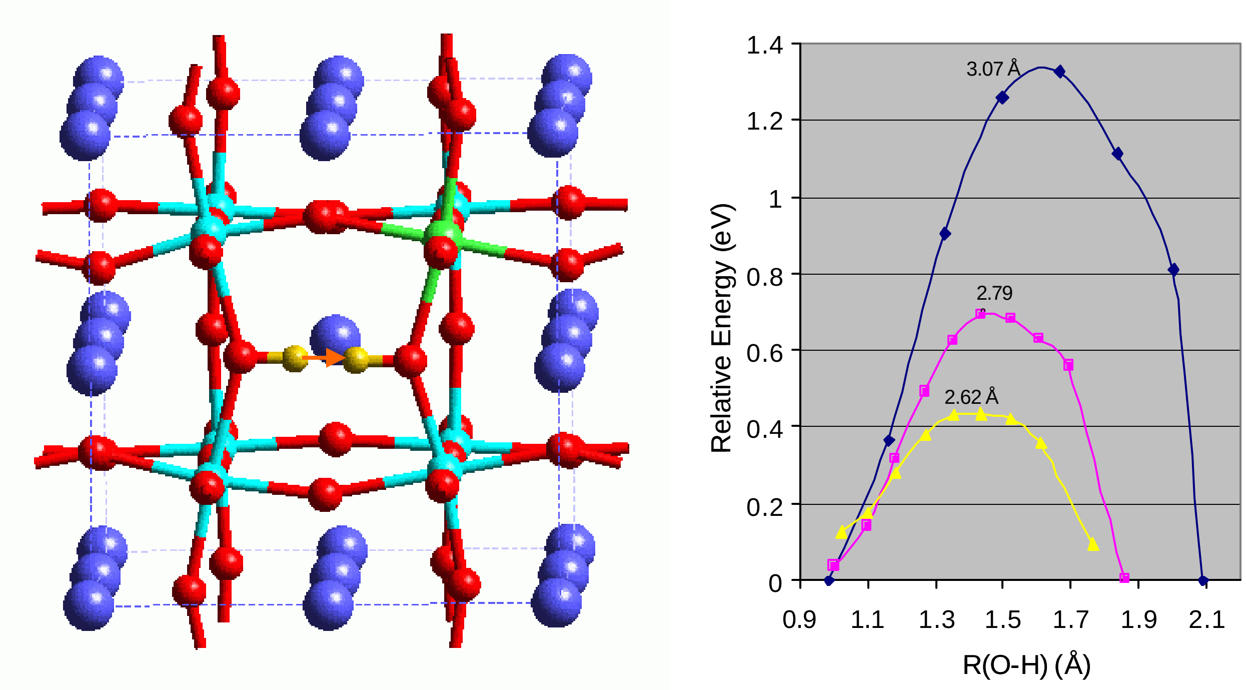

Figure 2. Inter-octahedra proton transfer in BYZ.
Left – BYZ structure (same notations as in Fig.1); right – energy barrier for inter-octahedra proton transfer.

We optimized the BYZ structure with hydrogen between two neighboring ZrO_6 octahedra and found the OH – O separation distance to be equal to 3.07 Å. For this distance the calculated energy barrier for the inter-octahedra proton transfer is 1.33 eV, which is significantly higher than the barrier for the intra-octahedron proton transfer. However, when we decreaseded the OH – O distance to 2.79 Å, the energy barrier for the proton transfer dropped to 0.58 eV, while the energy of the overall BYZ structure increased only by 0.04 eV. Further shortening the OH – O distance leads to the value of 0.31 eV for the proton transfer barrier, while the energy of the corresponding BYZ structure increases by 0.13 eV in comparison with that of the initial BYZ structure. Thus, the calculated activation energy for the inter-octahedra proton transfer can be estimated as 0.44 eV that is in perfect agreement with the experimental value (0.44 eV). Therefore, most probably the inter-octahedra proton transfer is observed in the BYZ electrolyte.

EXPERIMENTAL

Screen potential cathode materials (transition metal perovskites) and cathode electrocatalysts (metals) for reactivity with $BaZr_{1-x}Y_xO_{3-d}$, fabrication compatibility, and chemical stability in fuel cell environment.

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: $BaZr_{0.40}Pr_{0.40}Gd_{0.20}O_3$, $BaZr_{0.70}Pr_{0.10}Gd_{0.20}O_3$, $BaZr_{0.80}Co_{0.20}O_3$, $BaZr_{0.60}Y_{0.20}Co_{0.20}O_3$, $BaPr_{0.85}Y_{0.15}O_3$, $BaZr_{0.50}Pr_{0.30}Y_{0.20}O_3$, $BaZr_{0.60}Pr_{0.20}Y_{0.20}O_3$, $BaZr_{0.70}Pr_{0.10}Y_{0.20}O_3$,

All formed single phase perovskites as determined by X-ray power diffraction (data not shown). The Pr rich compound, $BaPr_{0.85}Y_{0.15}O_3$, however, proved to be unstable with time and at high temperature and was not considered further.

For the $BaZr_{0.8-x}Pr_xY_{0.20}O_3$ system only zirconium mole percentages of 50, 60, and 70 were considered because preliminary experiments show that $BaZr_{0.8-x}Pr_xY_{0.20}O_3$ with a zirconium content of less that 50 mole percent are unstable in atmospheres containing CO_2 (TGA data not shown here).

Potential cathodes were mixed with $BaZr_{0.85}Y_{0.15}O_3$ (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, $BaZr_{0.70}Pr_{0.10}Gd_{0.20}O_3$ and $BaZr_{0.80}Co_{0.20}O_3$ completely reacted with BYZ to yield a single, solid-solution perovskite phase and were not considered further. In contrast, mixtures of $BaZr_{0.40}Pr_{0.40}Gd_{0.20}O_3$ with BYZ and of $BaZr_{0.60}Y_{0.20}Co_{0.20}O_3$ with BYZ retained two perovskite phases, Figure 3, although the possibility of slight interdiffusion cannot be entirely ruled out.

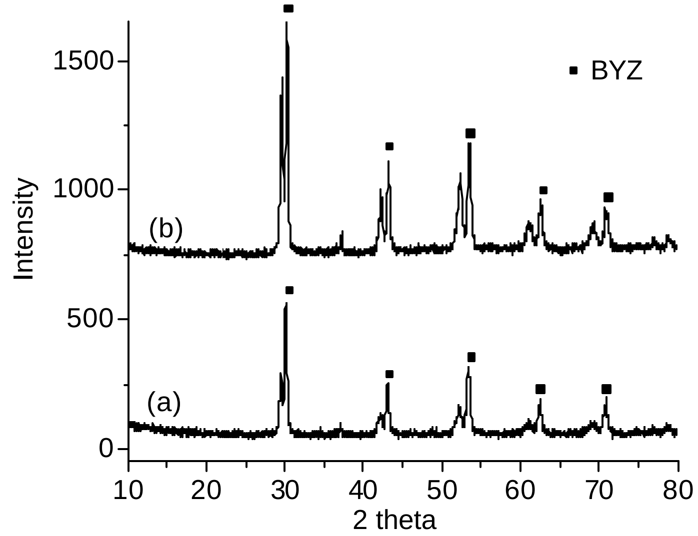

Figure 3. Diffraction patterns obtained from mixtures of (a) BYZ + $BaZr_{0.60}Y_{0.20}Co_{0.20}O_3$ and (b) BYZ + $BaZr_{0.40}Pr_{0.40}Gd_{0.20}O_3$, after exposure to 700°C for 24 hrs showing that two separate perovskite phases are retained.

The bulk conductivity of $BaZr_{0.40}Pr_{0.40}Gd_{0.20}O_3$, $BaZr_{0.60}Y_{0.20}Co_{0.20}O_3$, $BaZr_{0.50}Pr_{0.30}Y_{0.20}O_3$, $BaZr_{0.60}Pr_{0.20}Y_{0.20}O_3$, and $BaZr_{0.70}Pr_{0.10}Y_{0.20}O_3$ were measured by AC impedance methods in a wet air atmosphere, and is shown in Figure 4 and 5. $BaZr_{0.40}Pr_{0.40}Gd_{0.20}O_3$ and $BaZr_{0.60}Y_{0.20}Co_{0.20}O_3$ are promising materials because they have conductivity comparable to that of BYZ in the temperature range of interest. Surprisingly the activation energy of $BaZr_{0.40}Pr_{0.40}Gd_{0.20}O_3$ was measured as 0.40eV and $BaZr_{0.60}Y_{0.20}Co_{0.20}O_3$ 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.

The $BaZr_{0.8-x}Pr_xY_{0.20}O_3$ system with x =0.1,0.2,0.3 showed much lower conductivities than expected. It is believed the high resistively is most likely due to barium deficiency. The materials were sintered at 1600°C to prepare full dense sample for impedance measurements. Such high sintering temperature is needed due to the high zirconium content in the samples. Processing of the samples needs to be optimized (similar to the BYZ optimization) to suppress Ba loss during the sintering.

Further screening of cathode materials continues. Potential cathodes with sufficient conductivity will be deposited and tested on BYZ membranes.

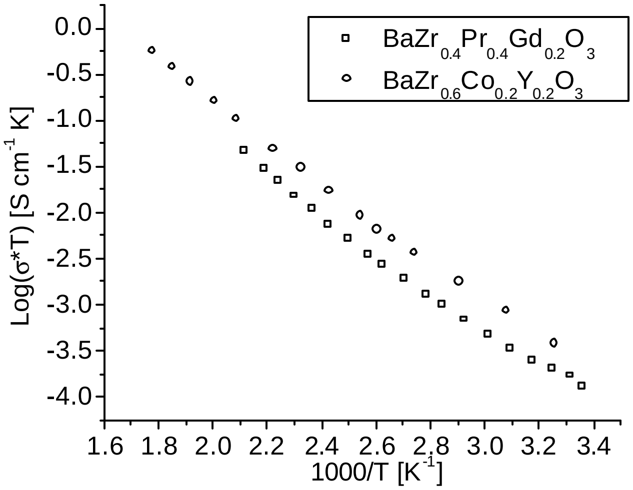

Figure 4. Bulk conductivity of two potential cathode materials as measured in wet air atmosphere.

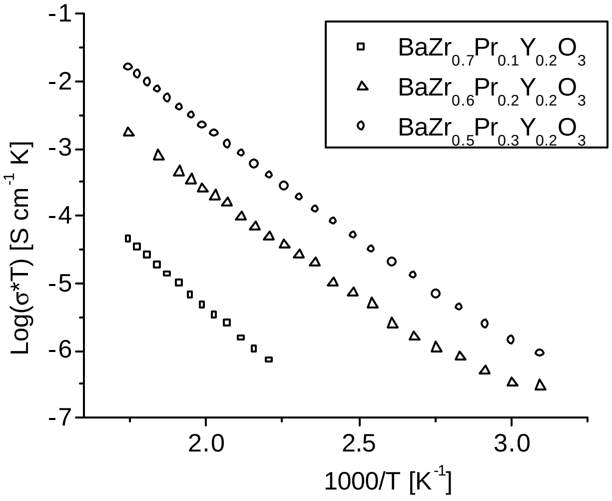

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Figure 5. Bulk conductivity of three potential cathode materials as measured in wet air atmosphere.

Screen potential anode electrocatalysts (metals) for reactivity with $BaZr_{1-x}Y_xO_{3-d}$, fabrication compatibility, and chemical stability in fuel cell environment.

Because Ni has been established as a good catalyst for anode reaction in YSZ, it was our initial intention to use a NiO-BYZ porous support for a thin BYZ electrolyte membrane.

However, according to our preliminary experiment, it was realized that NiO easily diffuse into the BYZ layer during sintering. Attempts were made to prevent this diffusion by lowering sintering temperature, however to obtain a high density layer sintering at 1600℃ is needed. Therefore, we concluded that it is very difficult to use NiO as support material. Then, we tried to find alternative support material that has catalytic ability for electrode reaction. In this study, FeOx, Ni, Fe and NiAl were examined, but all had fatal problem. Thus, we developed bi-layer and tri-layer BYZ systems with varying porosity. The support is a porous BYZ layer while the electrolyte is a fully densified layer. Figure 6 and 7 show SEM micrographs of such systems. Future plans include impregnation techniques to incorporate a metal catalyst into the porous layer.

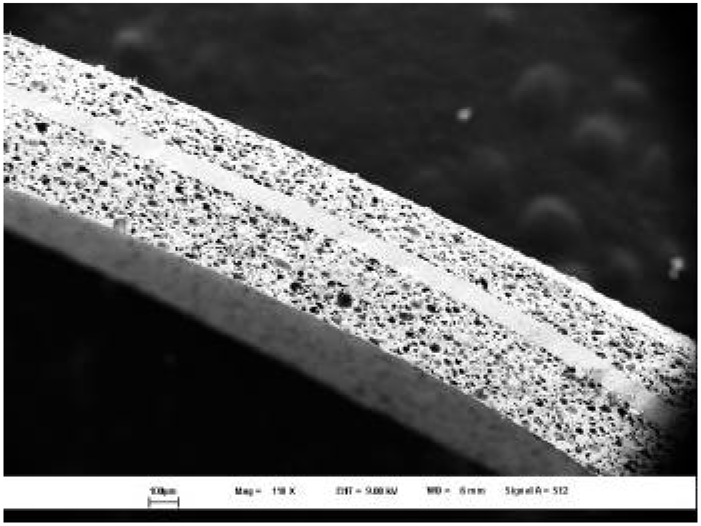

Figure 6. Cross section of 80 µm electrolyte BYZ membrane sandwiched by porous BYZ layers.

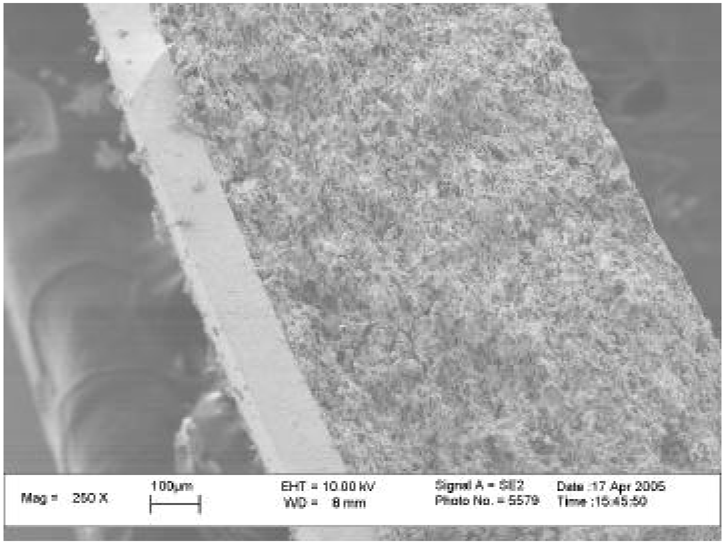

Figure 7. Cross-section of 100 µm electrolyte BYZ membrane on BYZ porous support.

CONCLUSIONS

A series of QM calculations on BYZ periodic structures have been performed and energy barriers for the proton diffusion have been calculated. The activation energy for the intra-octahedron proton transfer is found to be equal to 0.55 eV, while that for the inter-octahedra proton transfer is 0.44 eV, which is in perfect agreement with the experimental value, 0.44 eV.

According to our calculations the inter-octahedra proton transfer is mainly observed in the BYZ electrolyte.

Several potential cathode materials for the Y-doped $BaZrO_3$ system have been synthesized and characterized. Of the five potential cathode materials examined $BaZr_{0.40}Pr_{0.40}Gd_{0.20}O_3$ and $BaZr_{0.60}Y_{0.20}Co_{0.20}O_3$ appear to be the most promising for further applications in proton ceramic fuel cells.

Potential anode electrocatalysts (metals) have been screened for reactivity with $BaZr_{1-x}Y_xO_{3-\delta}$, fabrication compatibility, and chemical stability in fuel cell environment. It was found that NiO easily diffuse into the BYZ layer during sintering. Bi-layer and tri-layer BYZ systems with varying porosity have been developed.

REFERENCES

1. P.A. Schultz (unpublished). A description of the method is in P.J. Feibelman. *Phys Rev.* B**35**, 2626 (1987).
2. H.G. Bohn and T. Schober, *J. Am. Ceram. Soc.* **83**, 768 (2000).
3. W. Münch, K.-D. Kreuer, G. Seifert, J. Maier, *Solid State Ionics* **136-137**, 183 (2000).

LIST OF ACRONYMS AND ABBREVIATIONS

BYZ - $BaZr_{1-x}Y_xO_{3-\delta}$

MD - Molecular Dynamics,

PCFC – Proton Ceramic Fuel Cell,

QM - Quantum Mechanics,

ReaxFF - First Principles-Based Reactive Force Field,

SEM – Scanning Electron Microscopy

SOFC – Solid Oxide Fuel Cell

TGA – Thermo Gravimetric Analysis

XRD – X-ray Diffraction