

INTERIM REPORT

NETWORK-H2 CALL 2 - OPEN

PROJECT DETAILS

Grant number

NH2-005

Award holding organisation

Organisation

Imperial College of Science, Technology and Medicine

Title of research project

AmmoniaSHIP: Ammonia powered Ship with Proton conducting solid oxide fuel cells

Investigators

Role	Name	Organisation
Principal investigator	Dr Sivaprakash Sengodan	Imperial College of Science, Technology and Medicine
Co-investigator	Prof Stephen Skinner	
Co-investigator		
Co-investigator		

Grant number

NH2-005

Summary report – a summary of progress on the grant to date (up to 10 A4 pages)**Introduction**

Ships release considerable quantities of pollutants into the atmosphere, including nitrogen oxides (NO_x), sulphur oxides (SO_x), particulate matter (PM), and carbon dioxide (CO₂), which adds to acid rain and global warming. The marine commerce expands in lockstep with global population growth, and carbon dioxide emissions from the industry are predicted to increase by up to 250 % if no action is done.[1] Several alternatives exist for reducing shipping emissions, including the installation of a scrubber to remove SO_x and a selective catalytic reduction (SCR) reactor to remove NO_x. Another way to cut down on pollution is to change the internal combustion engine (ICE) or completely change the internal combustion propulsion system to an electric battery or fuel cell system. Hydrogen and ammonia fuels are gaining popularity as zero-carbon fuels because they can produce zero emissions when produced from renewable sources and can provide high power generation efficiency when used in fuel cell propulsion systems in marine ships. As a zero-carbon fuel, hydrogen has a high mass energy density. Fuel cells use hydrogen directly and these hydrogen fuel cells have been used in a number of shipbuilding projects. For example, a polymer electrolyte fuel cell (PEMFC) (60 kW) and battery hybrid ferry for 100 passengers was successfully built and operated by Alewijnse Marine Systems.[2] However, hydrogen continues to encounter several challenges, including a poor volumetric energy density, safety concerns, and storage constraints. When compared to hydrogen, ammonia has a lot more volumetric energy density and is easier to handle and store. In the study by Valera-Medina et al., they say that ammonia can cut the cost of storing it at least three times more than hydrogen can.[3] Another reason ammonia is better than hydrogen is that there is already a well-established supply chain and infrastructure because of the fertiliser industry. Kim et al. investigated and evaluated several ammonia systems for ship propulsion, including internal combustion engine (ICE), ammonia cracker with PEMFC, and solid oxide fuel cell (SOFC). It was found that SOFC systems based on oxide ion conductors were the most environmentally friendly, but they were also the most expensive and had the lowest power density.[4] In order to improve the electrochemical performance, durability, power density and other problems shown in oxide ion based SOFC's, we studied a fuel cell based on a proton-conducting solid oxide fuel cell (PCFC) for direct ammonia fuels for marine applications, as schematically shown in Figure 1. The efforts to build ammonia PCFCs are quite restricted, and the current results are unsatisfactory. Studies on the durability of ammonia PCFCs, in particular, are inadequate. As a result, further efforts are required to produce high-performance and long-lasting ammonia PCFCs.

The ammonia decomposition reaction is an endothermic process, and the full conversion of ammonia can be achieved at 500 °C and atmospheric pressure.[5][6] Hence, it is greatly feasible to utilize ammonia as a

fuel for PCFCs at relatively lower temperatures (500-700 °C) than oxygen ion-based SOFCs (O-SOFCs).[7][8] Steam is produced in the cathode in PCFCs, enabling high fuel utilization. In addition, since no oxygen ion is incorporated in the anode or electrolyte, no undesirable NO_x is formed.[9][10] When ammonia is supplied to PCFCs, ammonia utilization in the cell involves thermal and electro-catalytic processes that can be described as follows: adsorption of NH₃ on the anode surface, decomposition of NH₃ into H₂ and N₂, splitting of H₂ to monoatomic hydrogen, and electrochemical oxidation of hydrogen to a proton, and transport of the proton from the anode to the cathode, where H₂O is formed, as shown Figure 1.

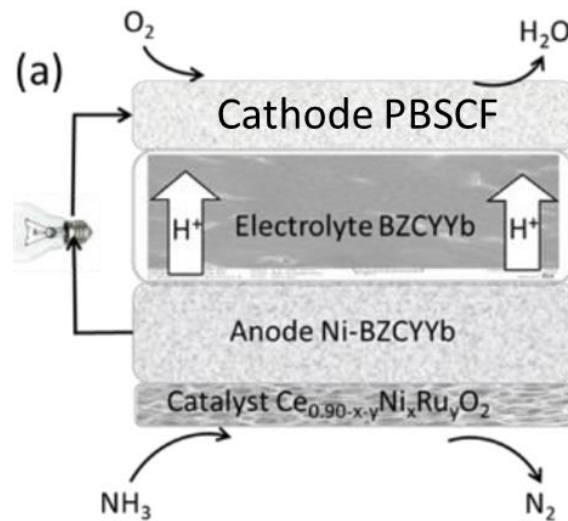


Figure. 1 Schematic of a fuel cell based on a proton-conducting electrolyte for direct ammonia fuels

However, many challenges still remain to significantly advance the PCFCs operated in NH₃, including the poor catalytic activity and stability of the state-of-the-art fuel electrode materials toward decomposition of ammonia, a lack of suitable cathodes designed for PCFC operation (typically between ~400 and 650 °C) and fabrication, inadequate proton conductivity of the electrolytes, instability of the interfaces, as well as variations in cell fabrication and testing. Furthermore, rapid degradation under typical operating conditions is a significant challenge for the development of fuel cells in NH₃. [11][12] To improve the anode performance, surface modification with nano-structured catalysts via a solution infiltration method has been used widely, providing more active sites and more choices for catalyst development. It was confirmed that tailoring the capabilities of NH₃ adsorption and N₂ desorption by forming alloys with a strong NH₃ adsorption and a weak nitrogen binding energy is an effective strategy to improve the cell performance. While surface modification is effective, the selection of suitable catalysts is critical to the performance and durability enhancement. To be effective in designing better materials for NH₃ utilization, it is necessary to gain deeper understanding of the reaction mechanism and elementary steps.

We also try to explore new cost-effective catalysts for ammonia dissociation in the fuel cell anode. We proposed that carefully designed Ru exsolved catalyst anode in solid oxide fuel cells based on a proton-

conducting electrolyte might be used to evaluate the electro-catalytic activity for ammonia dissociation: ammonia dissociates in the anode and then protons diffuse through the electrolyte to the cathode zone and subsequently react with oxygen species. The rate of hydrogen dissociation depends sensitively on the catalytic layer (similar to the anode in a fuel cell) deposited on the proton-conducting electrolyte. For cells with the same electrolyte and cathode, the difference in their performance is determined by the difference in the catalytic activity of the anodes for ammonia dissociation. If a cermet anode is used consisting of a metal phase (the catalyst) and the proton-conducting phase, the difference in cell performance may be determined mainly by the electro-catalytic activity of the metal catalyst loaded in the anode.

Experiment

Synthesis of BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_{3- δ} (BZCYYb4411) and NiO-BZCYYb composite powders

BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O₃ (BZCYYb) powders were synthesized by the typical solid state reaction method. Stoichiometric amounts of barium carbonate, zirconium oxide, cerium oxide, ytterbium oxide, and yttrium oxide powders (all from Aldrich Chemicals) were mixed by ball milling, followed by sintering at 1100 °C in air for 10 h.

Synthesis of PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O₅ (PBSCF) powder

Preparation of PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O₅ (PBSCF) powder PBSCF powder was prepared by a citric nitrate solution combustion method. Stoichiometric amounts of Pr(NO₃)₃, Ba(NO₃)₂, Sr(NO₃)₂, Co(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, were dissolved in DI water to form a solution of PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O. A stoichiometric amounts of citric acid (CA) and glycine were added as the complexing agent and the fuel for subsequent self-combustion. Metal ions: CA: glycine of 1: 0.75: 0.75. The powder was then fired at 900 °C for 2 h.

Fabrication of single cells

Ni-BZCYYb anode-supported cells were fabricated using the dropcoating method. NiO and BZCYYb powders (weight ratio of 6.5:3.5) were mixed by ball-milling in ethanol for 24 h. After drying, the NiO-BZCYYb mixture was pressed into a pellet (0.6 mm thick and 15 mm diameter). Thin BZCYYb electrolyte membranes were prepared by the refined particle suspension coating technique. A BZCYYb suspension was prepared by dispersing BZCYYb powder in ethanol with a small amount of binder (polyvinyl Butyral, B-98) and dispersant (triethanolamine, Alfa Aesar) at a ratio of 1:10. The BZCYYb suspension was applied to a NiO-BZCYYb anode support by drop-coating, followed by drying in air and subsequent co-sintering at 1400 °C for 4 h. For preparation of cathode slurries, presintered PBSCF cathode powders were mixed by ball-milling, blended together with an organic binder (Heraeus V006). The PBSCF cathode slurry was screen printed onto electrolyte surface of NiBZCYYb anode-supported cells. The single cells consisting three layers (PBSCF/BZCYYb/NiO-BZCYYb) were subsequently

sintered at 900 °C in air for 4 h.

Electro chemical testing

For the single-cell tests, Ag wires were attached at the cathode side using Ag paste and Pt wires were attached at the anode side using NiO paste as a current collector. The NiO-BZCYYb anode- supported single cell was sealed fully onto one end of the alumina tube using a ceramic adhesive (Aremco, Ceramabond 552). Humidified H₂ (3% H₂O) was applied to the anode side as a fuel through a water bubbler with a flow rate of 100 mL min⁻¹, while air was supplied as an oxidant to the cathode during the single cell test. The I–V polarization curves were recorded between 873 and 1023 K.

Results and discussions

Figure 2 shows the X-ray diffraction (XRD) pattern of BZCYYb powders calcined at 1500 °C for 24 h in air. Typical peaks corresponding to perovskite BZCYYb can be seen in the XRD pattern. The XRD patterns of PBSCF, and composite powders thereof are presented in Figure 1. The characteristic diffraction patterns of the PBSCF and composite powders are identified in a single phase, respectively. The chemical compatibility between the PBSCF and BZCYYb is investigated by heating the mixture at 900- 1000 °C for 12 h. As shown in Figure 1, there are no obvious reactions between the PBSCF and BZCYYb powders, indicating that the layered perovskite PBSCF is chemically compatible with BZCYYb under the present processing conditions.

Figure 3 and 4 presents SEM image showing the microstructure of the NBSCF cathode and a single cell (PBSCF/BZCYYb/NiO-BZCYYb), respectively. The PBSCF cathode has a highly porous morphology that ensures good gas diffusion. As shown in Figure 3, a dense BZCYYb electrolyte and a porous NBSCF cathode (about 15 mm thick) are successfully fabricated. The PBSCF cathodes adhered well onto the BZCYYb electrolyte without any cracks or delamination, which is expected to enhance the mechanical compatibility and the long-term stability of the cathode/electrolyte interface

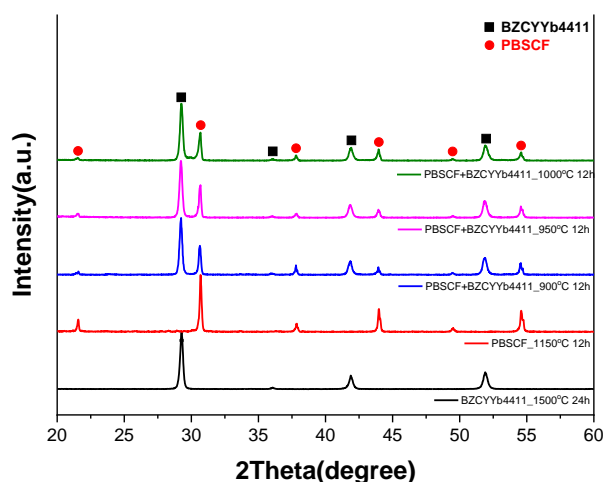


Figure. 2 XRD patterns of BZCYYB, PBSCF and BZCYYb + PBSCF powder calcined at different temperature in air.

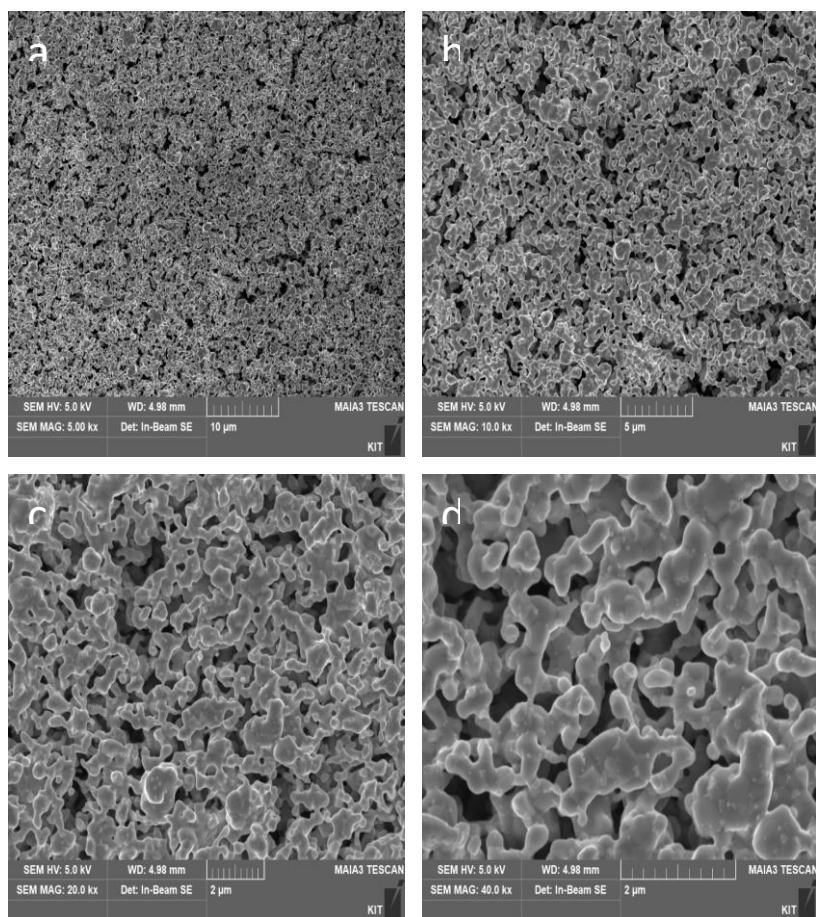


Figure. 3 Scanning electron microscope image of porous PBSCF cathode.

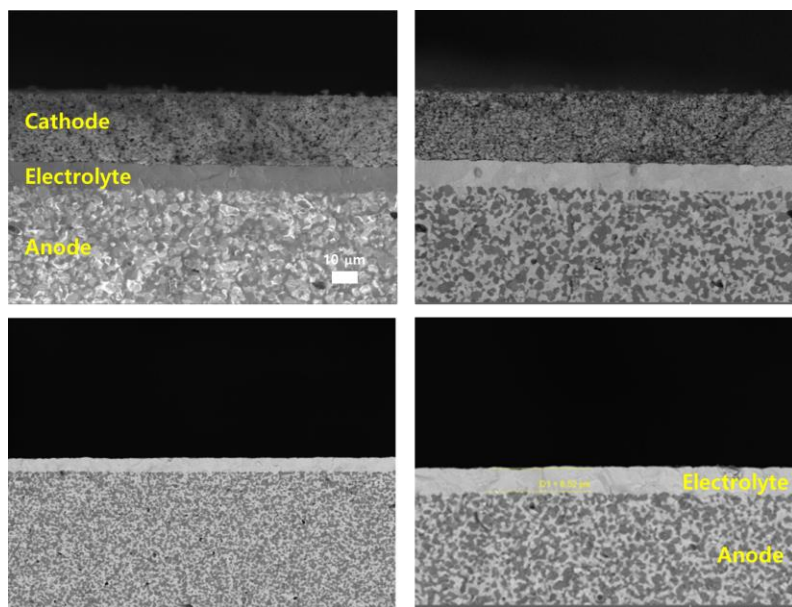
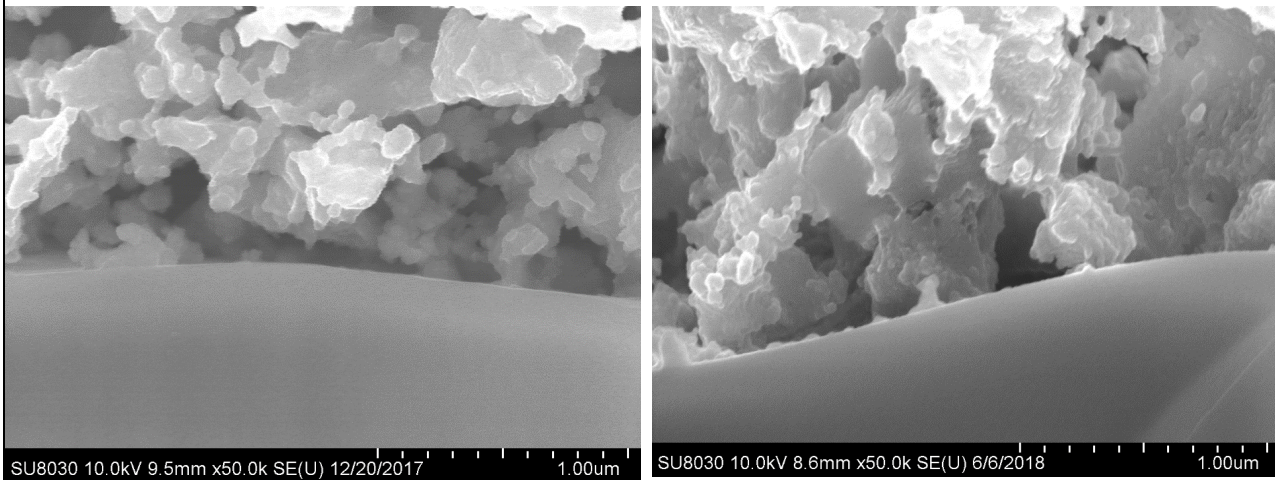


Figure. 4 Scanning electron microscope image of cross-section of the single cell.

Fig. 5 shows the cross section SEM image of (a) PBSCF cathode and (b) surface modified PBSCF cathode.



The electrochemical performance of the proton-conducting cell with PBSCF cathode and surface modified cathode is characterized by anode-supported cells based on a 250 mm thick BZCYYb/ NiO composite anode. In Fig. 6, the fuel cell performance of a single cell with PBSCF cathode and PBSCF surface modified PBSCF cathode. The final cell configuration is PBSCF/BZCYYb/NiO-BZCYYb. With the humidified (3% H₂O) H₂ as fuel, the peak power densities of the PBSCF cathode are 1.10, 0.79, 0.55, and 0.35, Wcm⁻² at 650, 600, 550 and 500 °C, respectively (Fig.6a). With the surface modified PBSCF cathode cell shows peak power densities of 1.64, 1.25, 0.88, and 0.53 Wcm⁻² at 650, 600, 550 and 500 °C, respectively (Fig. 6b)

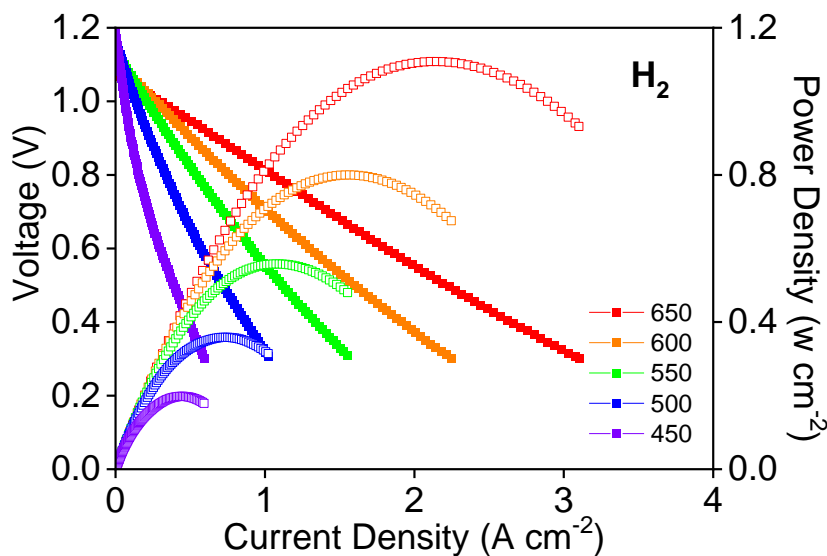


Fig. 6a. I–V curve and the corresponding power densities of PBSCF cathode in humidified (3% H₂O) fuels and ambient air as the oxidant.

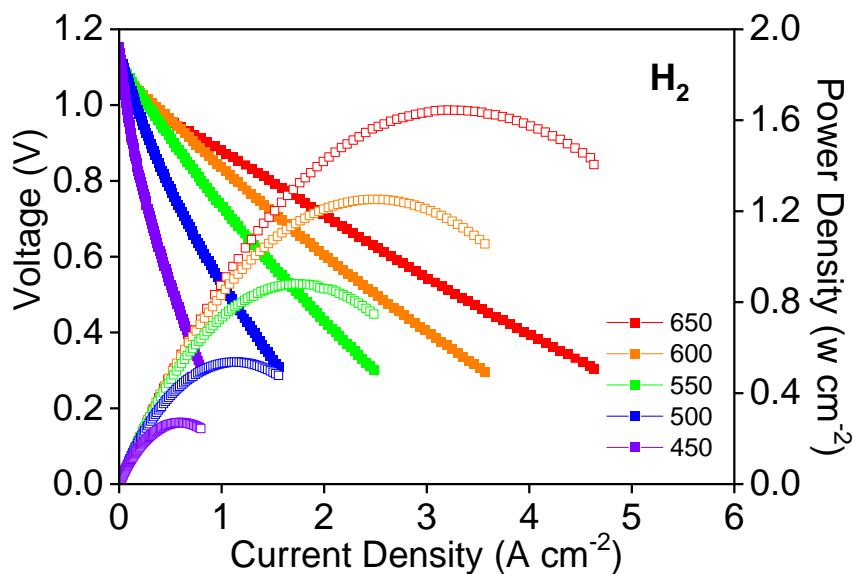


Fig. 6b. I-V curve and the corresponding power densities of surface modified PBSCF cathode in humidified (3% H₂O) fuels and ambient air as the oxidant

Conclusion

This research aims to find the most promising and suitable catalyst for ammonia fed PCFC for merchant vessels. A number of additional challenges should also be solved to prove the feasibility of ammonia as a ship fuel. First of all, the main potential drawback is the safety issue (corrosion, toxicity, low flammability, etc.). In terms of the materials development, we have fabricated PCFC based on BZCYYb electrolyte. A PCFC with a configuration of PBSCF/BZCYYb/BZCYYb-NiO single cells were fabricated to evaluate electrochemical performance in hydrogen. In summary, we evaluate the electrochemical performance PBSCF cathode and surface modified PBSCF cathode with a configuration PBSCF/BZCYYb/BZCYYb-NiO. The surface modified PBSCF cathodes effectively extend the electrochemically active sites from the interface between the cathode and the electrolyte to the entire surface of the cathode. This work demonstrates that the surface modified cathode PBSCF shows excellent compatibility with the proton-conducting electrolyte BZCYYb.

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