THESIS DEFENSE

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Date: 3/19/2018
Time: 3:00-5:00 PM
Location: HH300

Ceramic Electrochemical cells for power generation and fuel production

Abstract: New clean energy technologies with higher energy conversion efficiency and lower emission are required to address global energy and climate change challenges. Fuel cells have attracted a lot of attention in this vein due to their higher efficiency compared to conventional energy conversion technologies (e.g. heat engines). Among all fuel cell technologies, high-temperature solid oxide fuel cells (HT-SOFCs) exhibit various advantages compared with low-temperature polymer fuel cells including lower catalyst/cell costs, and high fuel flexibility. These advantages are mostly due to the high operating temperatures. Unfortunately, high operating temperatures also dramatically increase stack and system costs and decrease stability, thereby greatly hindering commercialization. Recently, a new class of ceramic fuel cells that can operate at lower temperatures than HT-SOFCs, but still at high enough temperatures to ensure high activity for hydrocarbon utilization has emerged. These fuel cells are based on ceramic electrolyte materials that are dominantly proton (rather than oxygen-ion) conductors. Because of the generally lower activation energy associated with proton conduction in oxides compared to oxygen ion conduction, protonic ceramic conductors can attain higher ionic conductivity at lower temperatures than oxygen ion conductors. Therefore, protonic ceramic fuel cells (PCFCs) should be able to operate at lower temperatures than solid oxide fuel cells (250-550 °C versus ≥600 °C) on hydrogen and hydrocarbon fuels if fabrication challenges and suitable cathodes can be developed.

Despite their promise, the poor sinterability of protonic ceramics (e.g. $BaZr_{0.8}Y_{0.2}O_{3-\delta}$) and the lack of specific cathodes with high oxygen reduction reaction (ORR) activity for PCFCs has led to much lower power densities for PCFCs compared to HT-SOFCs. In order to address these issues, this PhD thesis develops a novel solid state reactive sintering (SSRS) method that enables simplified PCFC fabrication directly from raw precursor oxides/carbonates using a suitable reactive sintering aide. In addition, this thesis develops a novel triple conducting oxide (mixed proton, oxygen-ion, and electron conductor), $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$(BCFZY0.1) for PCFC cathodes that greatly improves the ORR kinetics at intermediate to low temperatures. Highly durable PCFCs fabricated by the SSRS method with BCFZY0.1 deliver excellent power densities at intermediate temperatures and thousands hours of stable operation. In addition, we demonstrate remarkable fuel flexibility from our PCFC devices. Here results from long-term testing of PCFCs using a total of 11 different fuels (hydrogen, methane, domestic natural gas (with and without H_2S), propane, n-butane, i-butane, iso-octane, methanol, ethanol, and ammonia) at temperatures between 500-600 °C are presented. Several cells are tested for over 6000 hours, and we demonstrate excellent performance and exceptional durability (<1.5% degradation per 1000 hours in most cases) across all fuels without any modifications in the cell composition or architecture. In addition, sulfur and coking tolerance of PCFCs are studied by in-situ high-temperature Raman spectroscopy, which reveals that the relatively basic surface property of BZY can enhance its coking and sulfur tolerance. Based on these insights, BZY-surface species mediate coking and sulfur cleaning mechanisms are proposed in this work. The fuel flexibility and long-term durability demonstrated by the protonic ceramic electrochemical devices presented here highlight the promise of this technology and its potential for commercial application.

Finally, highly efficient reversible protonic-ceramic electrochemical cells (RePCECs) were developed by addressing challenges associated with low Faradaic Efficiency. RePCECs for energy conversion and storage enable versatile production and conversion of H_2, syngas, and hydrocarbon fuels with high Faradaic efficiency (>95%), high round-trip efficiency (71%), and long-term stable operation (degradation rate <50mV/1000 hours). Principles of materials selection and strategies for improve efficiency are detailed. Our protonic ceramic electrochemical device shows intriguing potential for the "green synthesis" of high-value chemicals from renewable electricity using only water, CO_2, and N_2 as input feedstocks.

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