

ABSTRACT

Effect of Hydration on Electrical and Electromechanical Properties of Lanthanum-Cerium Oxides

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In recent years, there has been a growing interest in the pursuit of efficient, clean, and environmentally friendly energy sources. Fuel cells have emerged as a promising technology, allowing the conversion of the chemical energy present in fuel gases into electrical work. Solid oxide fuel cells, which utilize ion-conducting ceramics as electrolytes, have been at the forefront of these developments. However, a significant drawback has been the high operational temperatures typically required, ranging from 300°C to 900°C, due to the thermally activated nature of ion conduction in ceramics.

All solid oxide fuel cells (SOFCs) and electrolyzers (SOEs) operating above 300°C demonstrate rapid electrode kinetics, especially those based on proton-conducting systems. However, they are limited in their long-term stability due to thermal stress. Ceramic devices operating between 150-250°C could enjoy rapid electrode kinetics, even without Pt-based catalysts, and would avoid large thermal stress. However, proton-conducting ceramics showing appreciable conductivity in this temperature range have yet to be identified. Developing such a material could revolutionize the field of renewable energy. We have investigated hydration of $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ (LCO) and found that for $x > 0.5$, it decomposes to $\text{La}(\text{OH})_3$ and CeO_2 upon contact with water or water vapor, limiting the search range to $x \leq 0.5$. LCO50 ceramics with steam or water-saturated nitrogen at 1 atm produces hydration up to $>4.4 \pm 1\%$ with respect to the theoretical limit. The hydration results in a 0.1% lattice expansion due to water incorporation and a large increase in electrical conductivity. Further hydration under these conditions results in the mechanical disintegration of the ceramic pellets due to three factors with opposing tendencies: (a) to achieve hydration within reasonably short experimental time (few days), oxygen vacancies in LCO must be mobile to transport water from the surface into the interior of the sample. This necessitates an increase in temperature, T , to increase vacancy mobility; (b) increase in temperature shifts the solid - water vapor equilibrium towards dehydration (~ 350 C at $\text{PH}_2\text{O} = 1$ atm); (c) increase in PH_2O counteracts the heating by promoting hydration at the surface but increases the strain gradient. Therefore, for each composition there is a narrow range of $T - \text{PH}_2\text{O}$ to achieve hydration without mechanical disintegration.

We have developed a small ($<4 \text{ cm}^3$) hydration chamber with chemically fixed PH_2O , which permits the hydration of bulk (mm-sized) ceramic samples while preserving their mechanical integrity. The absence of crack and fissures due to hydration was verified using Ultra-Sound-Time of Flight (USTOF) measurements, which were also used to measure changes in the elastic moduli resulting from hydration.

It was found that for $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ $x < 0.4$, no hydration takes place at any (T, PH_2O) combination. We have succeeded in achieving 23% hydration for LCO50, 22% of hydration for LCO45, and 5% for LCO40, corresponding to 0.52%, 0.4% and 0,08% expansions of the lattice. Hydration causes small but noticeable increases in the Young's modulus and has little effect on electrostriction coefficient, which is the opposite behavior to that observed upon hydration of acceptor doped BaZrO_3 .

Hydration causes a several-fold increase in the electrical conductivity of the samples. However, proton mobility is estimated to be at least three orders of magnitude lower than in Y-doped BaZrO_3 at 190°C . Importantly, no blocking effect of grain boundaries in LCO was observed, making it attractive for further studies leading to viable proton conducting ceramics suitable for use in bulk form or as micro-fabrication-compatible thin films.