Study of the Thickness and Temperature Dependence of the Ionic Conductivity of Hf$_{0.05}$Si$_{0.95}$O$_2$ Nano-Films

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With today’s rising energy costs it is essential to further develop alternate energy sources like fuel cells. Fuel cells that operate at intermediate temperatures between 200 and 400°C, IT-FC, are of particular interest, since this temperature range allows for uses of less precious metal catalysts and alcohol fuel and facilitates simpler module assembly. Thin films of inorganic proton-conductors show promising potential as electrolyte membranes of IT-FC. Here, we study the proton conductivity of nanometer-thick films of amorphous hafnium silicate, Hf$_{0.05}$Si$_{0.95}$O$_2$. Hf$_{0.05}$Si$_{0.95}$O$_2$ films are prepared from the precursor sols of Hf(OC$_4$H$_9$)$_4$ and Si(OC$_2$H$_5$)$_4$ in 1-propanol. Total metal concentration of precursor the sols is were adjusted as to 40mM and 100mM. The precursor sols were spin-coated on an indium tin oxide (ITO) coated glass substrate, and the deposited layer was hydrolysed by hot-wet-air-browning for a few minutes. These cycles of spin-coating and hydrolysis were repeated 10-20 times and the gel film thus obtained was calcined at 400°C for 15 min. These cycles of deposition and calcination were repeated more than 3 times, and the final calcination was performed at 430°C for 1 h. The samples were then cut into smaller pieces and platinum electrodes (1 mmφ) were deposited through a mask by magnetron sputtering in order to form a Pt/film/ITO stack. The conductivity across the film was measured by impedance spectroscopy by changing temperature and thickness. The thickness of the samples was determined by cross-sectional scanning electron microscopy (SEM). Sub-100 nm-thick Hf$_{0.05}$Si$_{0.95}$O$_2$ films show enhanced protonic conductivity at higher temperatures (300°C-400°C). Futhermore, the ionic conductivity of Hf$_{0.05}$Si$_{0.95}$O$_2$ film at elevated temperatures increased with decreasing thickness, and conductivity of 80 nm-thick films at 300°C is 10-fold higher than that of the 200 nm-thick. The scaling behavior of the conductivity of the film can be related to the finite size scaling of the percolative cluster to form ionic channels in an oxide glass network.
Solid Oxide Fuel Cell

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Introduction:

Fuel cells today are usually one of two types: polymer-electrolyte (PEFC) and solid oxide fuel cells (SOFC). However, there is a somewhat large gap in the temperature ranges in which these types of fuel cells can work effectively. Fuel cells which can operate within the intermediate temperature range of 200-400°C are desirable as a multipurpose fuel cell system, due to their durability and robustness. Suitable ceramic electrolytes are still being developed.

Objective:

The objective of this study is to investigate the ionic conductivity of Hf$_{0.05}$Si$_{0.95}$O$_2$ thin films and observe the effects of the finite size scaling of the percolation system at various temperatures.

Experimental:

Preparation of Hf-Si mixed precursor sol (Hf/ Si = 5/95)

Results:

Summary and Conclusions:

- Hf$_{0.05}$Si$_{0.95}$O$_2$ films were made on ITO glass substrates on the nanometer scale.
- Impedance spectroscopy was successfully run on samples in order to determine proton conductivity.
- The 100 and 130nm samples showed roughly the same proton conductivity. However, the 80nm sample showed significantly higher proton conductivity.
- This data supports the finite scaling of a percolation system.

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