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 $Hf(OC_4H_9)_4$ and $Si(OC_2H_5)_4$ in 1-propanol. Total metal concentration of precursor the sols iswere adjusted asto 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-browing 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^oC-400^oC). 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 highere 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.

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Introduction:

Fuel cells today are usually one of two types, polymerelectrolyte (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 in the intermediate temperature range of 200-400°C are desirable as a multipurpose fuel cell system, because this temperature range allows for the use of inexpensive materials including non-noble metal catalysts and normal stainless-steel components and may enable *in situ* reforming of hydrocarbons and biofuels (ethanol). In this temperature range, SOFC are more suitable than polymer-electrolyte fuel cells due to their durability and robustness. Suitable ceramic electrolytes are still being developed.

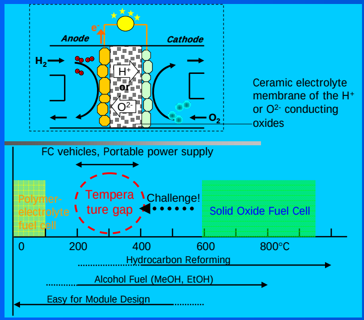

Figure 1: Current fuel cells

One possible solution to this problem was recently investigated by Yoshitaka Aoki et. al. It is a phenomenon called finite size scaling of a percolation system. Simply put its says that if there is a 3D matrix of points with a certain percentage of conducting points, the probability of a complete pathway across the system increases as the size of the system decreases.

In this study, $Hf_{0.05}Si_{0.95}O_2$ was chosen because it was predicted to also demonstrate this phenomena and due to its amorphus nature and decent chemical activity, making thin films with it was easier

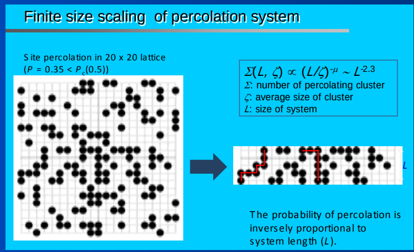

Figure 2: Diagram of percolation system

Objective:

The objective of this study is to investigate the ionic conductivity of Hf0.05Si0.95O2 thin films and observe the effects of the finite size scaling of the percolation system at various temperatures.

Experimental:

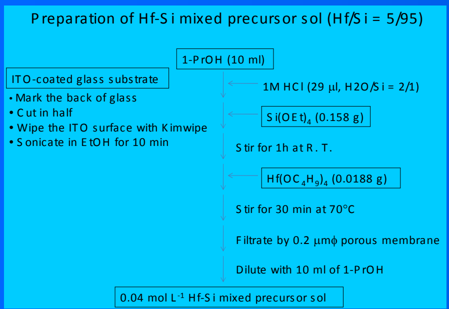

Figure 3: Process for preparation of precursor sol

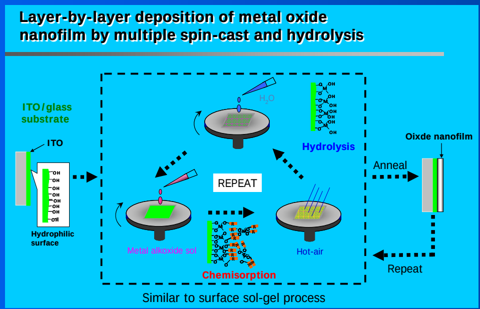

Figure 4: Sol-gel spin coating method

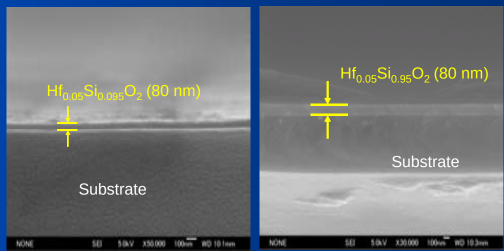

Figure 5: SEM images of the 80 (left) and 130nm(right) samples

Results:

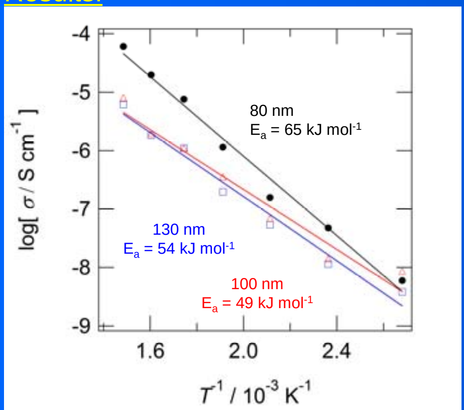

Figure 6: Arrhenius plots of proton conductivity across the $Hf_{0.05}Si_{0.95}O_2$ nanofilms

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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