

## V.P.30 Proton Conduction in Rare-Earth Phosphates

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### Objectives

The program aims to design, synthesize and test rare earth phosphate materials for proton conducting applications in the temperature region of 300-550 degrees Celsius. The program relies on three major approaches: a theoretical understanding of proton conduction in rare earth phosphates employing quantum chemical computation and molecular simulation; the chemical design, synthesis, and proton conductivity measurement of nano-composite materials expected to exhibit facile proton conduction; and the structural and dynamical characterization of the nano-composite materials using a range of advanced characterization methods including nanoscale structural and chemical electron microscopy, vibrational and x-ray spectroscopy, and nuclear magnetic resonance (NMR).

### Technical Barriers

Hydrogen, as well some biofuels, can be advantageously used for electric power generation in fuel cells that can operate between 350- 550°C, significantly lowering materials cost, simplifying catalysis, and extending fuel cell lifetimes. An essential component to enable this technology is the development of appropriate proton conducting membranes. However, these membranes are not presently available. This program examines the fundamental aspects of proton conduction in doped rare earth phosphates to provide such membranes.

### Abstract

Lanthanum and Cerium phosphates with modified grain boundaries were synthesized and characterized, showing proton conductivity in amorphous, nanometer grain boundary layers as high as  $10^{-3}$  S/cm at 500°C. First principles computation revealed that proton

conduction in rare earth phosphates, such as  $\text{LaPO}_4$ , proceeds by intertetrahedral hopping. Temperature-dependent  $^1\text{H}$  MAS-NMR results below 150°C confirmed computed proton activation energies for local motion. It was shown that dramatic increases in proton conductivity in La-phosphates resulted from the introduction of Al, Sr, and Ca leading to glasses and glass-ceramics conductors with a conductivity of  $\sim 10^{-4}$  S/cm at 440°C in dry argon, a record to date. The  $(\text{LaSrAl})\text{P}_x\text{O}_y$  glasses have a melting point of about 800°C, and can allow for easy membrane production by common glass processing methods, and may be thermally manipulated further to yield nanocomposite glass-ceramics with even higher expected conductivities. This finding points to way to easily-fabricated thin proton conducting membranes for hydrogen/air fuel cells operating in the technologically advantageous range of 300-500°C.

Structural and functional characteristics determined by TEM, NMR, and Raman and IR spectroscopy of doped La-phosphate glasses have indicated, for the first time, that proton trapping at aliovalent dopants can play a significant role in determining proton conductivities.

### Progress Report

The electrical properties of  $[\text{La}_{(1-x)}\text{M}_x]\text{-P}_3\text{O}_9$  metaphosphate glasses, where M is Ba, Sr, Ca, and  $0 \leq x \leq 0.8$  were investigated in the 300 – 500°C range. The protonic conductivity increases two orders of magnitude from the unsubstituted to the 60% substituted glass reaching a maximum conductivity of about  $10^{-5}$  S/cm at 450°C. The activation energy is found to be approximately independent of concentration though dependent on the type of modifying substitutional cation, and decreases from about 1.04 eV for Ca and Sr to  $\sim 0.96$  eV for Ba. AC impedance measurements were used to find the DC ionic conductivities. Mean ion travel distances at the frequencies,  $\nu_Z^*$  or  $\nu_M^*$ , associated with the maximum in  $Z''$  or  $M''$  were found to be up to 30 times larger than the average oxygen spacing in the glasses. While diffusion coefficients derived from conductivities,  $D_\sigma$ , were vastly lower than an uncorrelated diffusion coefficient computed from first principles, the travel distance at  $\nu_Z^*$  or  $\nu_Z^*$  derived from a simple random walk expression using  $D_r$ , were surprisingly close to those derived from the more rigorous statistical treatments. The ratio  $\xi = D_\sigma / D_r \ll 1$  may be interpreted as indicative of highly correlated ion motion and strongly reduced mean attempt frequencies, together with a mean activation energy for motion increased by  $\Delta E = E_\sigma - E_r$  over that of the uncorrelated intertetrahedral motion of an ideal crystal characterized by  $D_r$ .

$\text{Al}_2\text{O}_3$  was added to a  $2\text{CaO-La}_2\text{O}_3-5\text{P}_2\text{O}_5$  metaphosphate, to replace 10% of the  $\text{Ca}^{2+}$  ions by  $\text{Al}^{3+}$ , forming a phosphate with the nominal composition  $1.8\text{CaO}-0.1\text{Al}_2\text{O}_3-\text{La}_2\text{O}_3-5\text{P}_2\text{O}_5$ . The effect of  $\text{Al}_2\text{O}_3$  addition and heat treatment on the microstructure and conductivity of the resulting glass-ceramics was investigated by XRD, SEM, TEM, and AC impedance spectroscopy. Upon transformation from glass to glass-ceramic, conductivities increased significantly. The glasses were isochronally transformed at 700 and at 800°C for 1 hr or 5 hrs, in air, following heating at 3 or 10°C/min. With  $\text{Al}_2\text{O}_3$  addition, after a heat treatment at 700°C, 100~300 nm nano-domains of  $\text{LaP}_3\text{O}_9$  crystallized from the glass matrix. Annealing at 800°C produced a further order of magnitude conductivity increase for the Al-free glass, but less so for the Al-containing glass.

Structural and electronic properties of cerium orthophosphate ( $\text{CePO}_4$ ), a mixed electronic and protonic conducting electrolyte, are calculated using density functional theory (DFT) and beyond, and compared with experiments. A Hubbard-like parameter  $U$  is employed to reduce the self-interaction for localized Ce 4f states. As  $U$  is varied from 1-5 eV, the band structure is found to undergo significant changes, with the Kohn-Sham gap varying between 0.8 and 4.3 eV. Interestingly, the lattice parameters are unchanged, indicating structural properties are far less sensitive to  $U$ . The valence band energies and the optical band gap of  $\text{CePO}_4$  are measured using photoemission and optical reflectance spectroscopy. The structure was determined using XRD. The choice of  $U = 3$  eV provides the best match between the calculated density of states and the experimental photoemission and optical reflectance spectra. The activation energy of the minimum energy path for proton transfer will be calculated and compared to that of  $\text{LaPO}_4$ , another proton conducting electrolyte.

Rare earth phosphate ceramics have been investigated as proton conductors for applications in fuel cells, hydrogen sensors, and hydrogen separation membranes. Protons are incorporated into the materials as charge-compensating defects when the phosphates are doped with aliovalent cations. Protons bond to oxygen atoms on the phosphate tetrahedra and are thought to move through the material via intertetrahedral transfer. Lanthanum orthophosphate ( $\text{LaPO}_4$ ), a monoclinic material with space group  $\text{P}2_1/\text{n}$ , is an established proton conductor of this type. When doped with 1-2 mol. % strontium,  $\text{LaPO}_4$  exhibits a total conductivity on the order of  $10^{-5}$  S/cm at 500°C under both oxidizing and reducing conditions.

Cerium orthophosphate ( $\text{CePO}_4$ ) ceramics are almost structurally identical to  $\text{LaPO}_4$ . However, they demonstrate an interesting change in total conductivity when subjected to different atmospheric conditions. AC impedance measurements have shown the conductivity of 2% Sr-doped  $\text{CePO}_4$  at 500°C to be  $10^{-4}$  S/cm in

wet hydrogen, but to increase nearly two orders of magnitude to  $10^{-2.5}$  S/cm in wet air. The open circuit voltage of  $\text{CePO}_4$  in a fuel cell setup is found to be 0.25 V at 500°C, much lower than that expected from a pure proton conductor. This behavior is thought to be due to mixed proton and hole conductivity. Under reducing conditions, proton conductivity is thought to dominate, whereas under oxidizing conditions, the carrier is thought to be electron holes.

### Future Directions

- Doped nanocomposite RE-phosphates are synthesized from quenched glass melts, by controlled thermal annealing to manipulate the glass-ceramic nucleation and growth, to exploit conductivity enhancement that can result from such architectures.
- First-principle calculations at NERSC in conjunction with conductivity measurements and heteronuclear correlation and pulsed gradient NMR are used to elucidate the proton conduction mechanisms.
- Advanced high resolution chemical and structural characterization carried out in the facilities at the National Center for Electron Microscopy and the Molecular foundry to support NMR and vibrational spectroscopy studies.
- AC and DC conductivities are measured on the REP glasses and glass ceramics as a function of composition and water vapor exposure, to determine the proton transference numbers.
- Detailed structural elucidation of the nanocomposite materials is done using several multidimensional and multi-quantum NMR techniques, with an emphasis on understanding the impact of aliovalent substitution on proton dissolution in rare earth phosphates.

### Publications

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