Conductivity of $NdPO_4$-CsH_2PO_4 composites

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Outline

The introduction of alternative materials enables fuel cells to operate at higher temperatures and this would have a great influence on the successful commercialization of fuel cell technology. Considerable effort has been devoted to developing such proton conductors worldwide. Phosphates have a wide range of potential applications either in the form of powders, coatings or dense sintered parts. Conductivity can vary by more than ten orders of magnitude, sometimes over a temperature interval of only a few degrees. In materials containing ionic bonds, the defects are charged naturally and therefore ionic transport is synonymous with ionic conduction.

Solid salt conductors, based on phosphates powders, have received attention as novel electrolytes in fuel cells. Compounds within this class exhibit proton transport with conductivities high enough at temperatures 120-300 ºC. We have investigated phosphates mixed powders of CsH_2PO_4 and $NdPO_4$containing crystalline water as potential application for the solid state proton conductors by using electrochemical impedance technique. The proton conductivity of rare earth phosphates can be improved by sintering them with the ideal microstructure.

Experimental

We prepared the series of samples of $NdPO_4{\cdot}nH_2O$ (structure have shown Fig.1), CsH_2PO_4 and their composites with different mass ratio.

The electrochemical impedance spectroscopy (EIS) measurements was done using potentiostat VersaStat 4 with Versa Studio software at different temperatures with constant partial pressure and at different partial pressures with constant temperature. Conductivity values Fig. 2 and Fig. 3 were calculated from EIS pictures using real part of impedance versus frequency.

Fig.1 shows view of $NdPO_4{\cdot}nH_2O$ structure along the c-axis. $NdPO_4$ hexagonal modification. Nd^{3+} ions shown in red and purple and PO_4 tetrahedral shown in yellow.

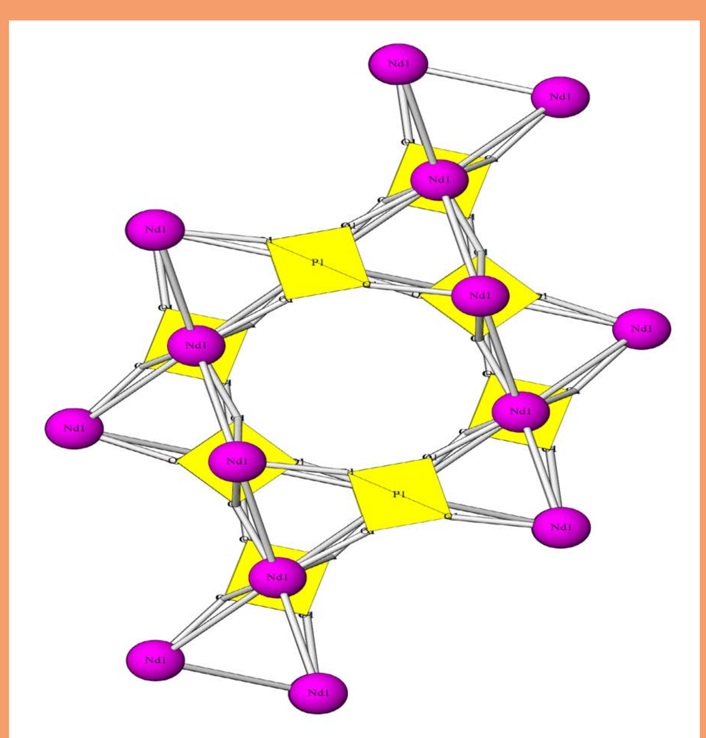

Fig. 1. Structure of $NdPO_4$ (rhabdophane structure)

The relevant distances for $NdPO_4$ were measured from crystal structure, which was prepared in Atoms63™ using reported data. The crystal structure of $NdPO_4$ as seen along c-axis is shown in Fig.1. It consists of isolated tetrahedra of PO_4 which are held together by Nd^{3+}cations. Each Nd^{3+} cation is surrounded by nine oxygen ions.. The location of water molecules is suggested by geometrical considerations.

The conductivity (σ) of the disc was given by:

$$\sigma = \frac{L}{R \cdot A}$$

where L, R, and A are the thickness, the resistance and the cross-sectional area of the disc, respectively.

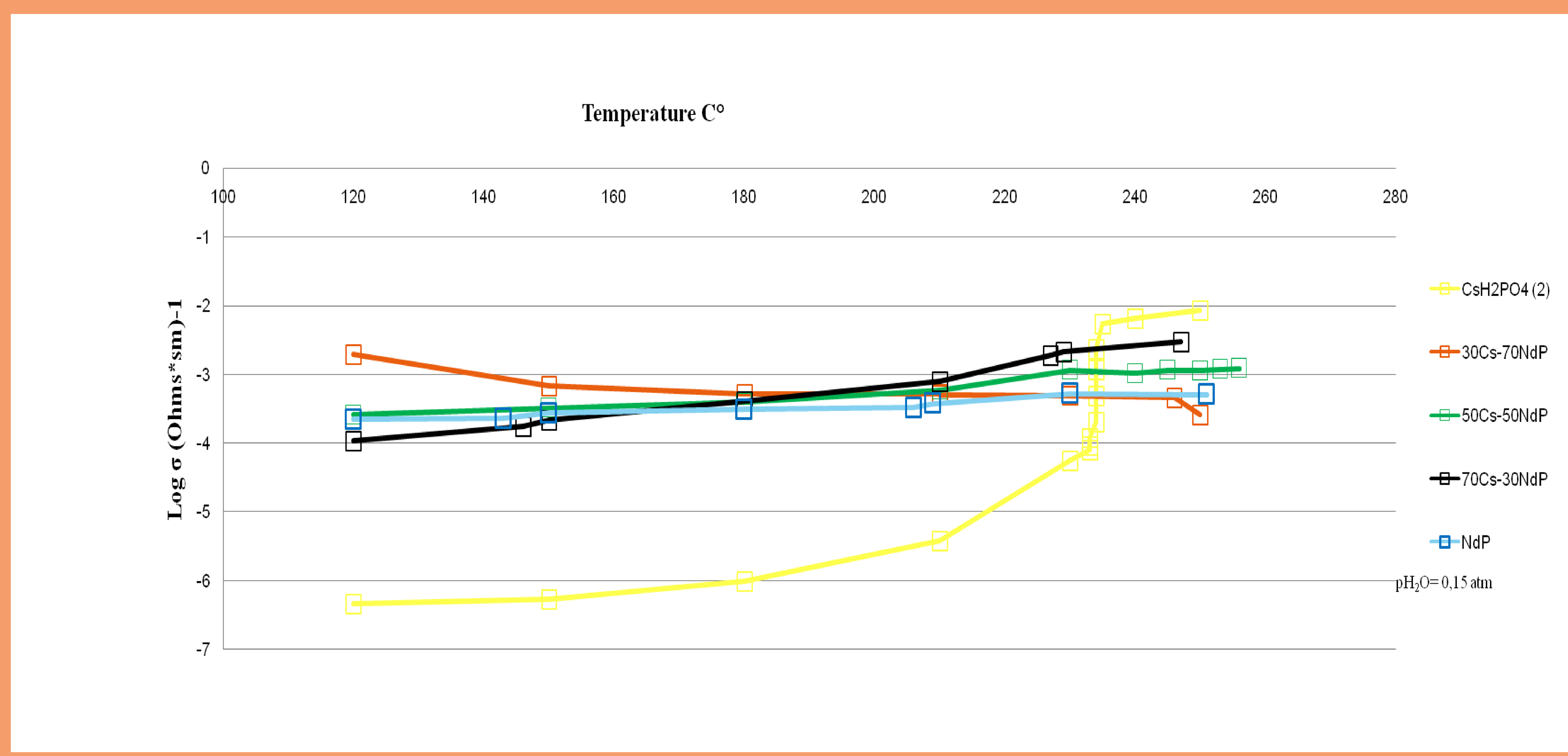

Fig. 2. Conductivity of CsH_2PO_4, mixed composites and $NdPO_4{\cdot}nH_2O$ at different temperatures from 120 C° to 250 C° with constant humidity (P_{H2O}= 0,15 atm.)

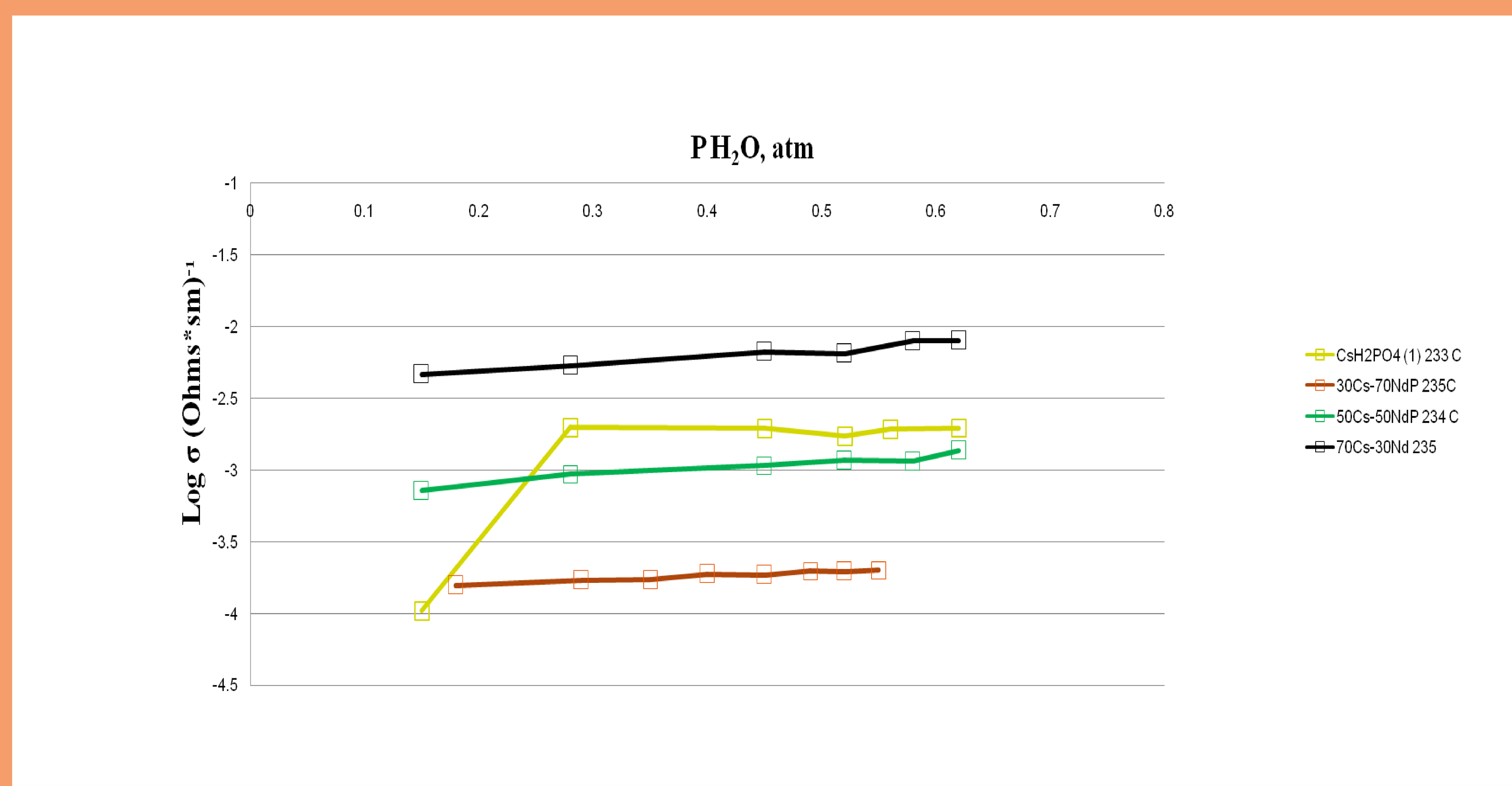

Fig. 3. Conductivity of CsH_2PO_4 and mixed composites at temperature approximately 235 C° with different humidity content.

The sample of composite 70 % mass. CsH_2PO_4 and 30 % mass. $NdPO_4{\cdot}nH_2O$ have shown the most interesting conductivity properties at 235 C°.

References

[1] Proton conductors. Solids, membranes and gels materials and devices edited by Philippe Colomban. Cambridge University Press (1992)

[2] S. Lucas, E. Champion, D. Bregiroux, D. Bernache-Assollant, F. Audubert, J. Solid State Chem. 177 (2004) 1312–1320.

[3] J.A. Diaz-Guillen, A.F. Fuentes, S. Gallini, M.T. Colomer, J. Alloys Compd.427 (2007) 87–93 4154–4161.