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Highly Proton Conducting Composite for Fuel Cell Applications

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Abstract – We report on phase and proton behaviours of (1-x)$(NH_4)H_2PO_{4-xTiO2}$ ($x \leq 0.1$) composites by thermal analysis and impedance spectroscopy, in the radio frequency range and at temperatures between 303 and 563 K. Simultaneous thermal and electrical measurements on the composites identifies three different regions of phase behaviour: region (I) from 303 to 373 K, followed by a mid- and high-temperature regions (II, $373<T\leq463$ K and III, $463<T\leq523$ K, respectively). The activation energy of the dc conductivity decrease from 0.55 eV to 0.35 eV as the concentration of the nanoparticles of TiO_2 increases. The highest dc-conductivity is obtained for the composite with concentration x=0.05, with values above room temperature that are about 3 orders of magnitude higher that that of crystalline ADP, reaching values of the order of 0.1 $(\Omega cm)^{-1}$ above 523 K. The results for region II (a stable phase of ADP) are explained considering that the nanocrystalline powders TiO2 having the average grain size of 50 nm modify the macroscopic proton transport in ADP due the enhancement of structural disorder in the interfaces of nanoparticles with the ADP solid matrix.

The different sample compositions were prepared from $NH_4H_2PO_4$ 99.999% powder, (Aldrich) and TiO_2 nanoparticles powder (Aldrich, 99.8% trace metal basic, < 50nm (XRD) by thoroughly mixing molar ratios (x) of components in an agate mortar and then heated for 12 hours at 423 K, close and below to the reported dehydration reaction of ADP.

Differential scanning calorimetry (DSC) was performed with a TA Instruments 2920 Modulated DSC with a temperature scan of 10 K/min and under a dry N_2 flux. The electrical characterization of the samples was done by impedance spectroscopy (IS) using a two electrode configuration Pt|sample|Pt and a home-built temperature and atmosphere controlled cell for measurements. The measuremets were carried out with a computer controlled Agilent 4294A LCR meter in the frequency range of 40 Hz -13 MHz, in the isothermal or in the heating cooling modes, at temperatures between $303 \leq T \leq 553$ K. The real part of the conductivity was well described by the Jonscher´s expression $\sigma' = \sigma(1+(\omega/\omega_p)^n)$ where σ is the dc conductivity, ω_p is a characteristic relaxation frequency, and n is a fractional exponent between 0 and 1. The results show that all the transport parameters (exponent, n, the crossover frequency, ω_p, and the dc-conductivity, decrease with increasing temperature up to 373 K, where the DSC curve shows a small endothermic peak. This behavior may be associated with a dehydration process on the surface of the sample, such that, at 373 K, this reaction is completed. This region is followed by a stable phase up to 463 K in which the dc-conductivity and the crossover frequency are equally activated, indicating similar mechanism (ion jumping) for both processes. Finally, above 523 K a highly conducting and viscous phase is found with dc conductivity values of the order of 0.1 $(\Omega cm)^{-1}$, comparable to a good liquid electrolyte.

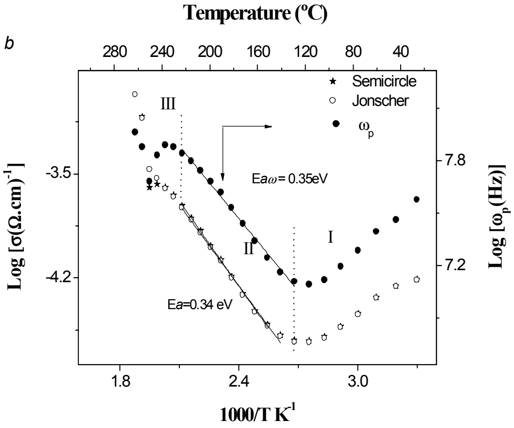

Figure 1: Arrhenius plots of the temperature dependence of the dc-conductivity(σ) and crossover frequency (ω_p), for the (a) $0.95(NH_4)H_2PO_4$-$0.05TiO_2$

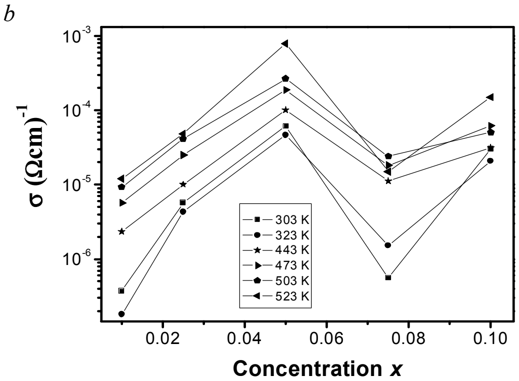

Figure 2: Concentration dependence (x) of the dc-conductivity (σ) *for* the (1-x) $(NH_4)H_2PO_4$-$xTiO_2$ composites at temperatures between 313 and 523 K [1]

[1] J. Castillo, et al., Ionics 15 (2009) 329.