

New Inorganic-Organic Polymer Electrolytes based on Polyethylene Glycol 400 and Aluminum Isopropoxide: Conductivity Mechanism, Thermal Stability and Morphology (part II).

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In this report are presented accurate studies on the morphology, thermal stability and electrical spectroscopy of eleven aluminum containing hybrid inorganic-organic polymer electrolytes of the ORMOCERS-APE type^[1] with general formula $\{Al[(CH_2CH_2O)_{8.671}]_p/(LiClO_4)_z\}_n$, where $1.85 \leq p \leq 2.24$ and $0 \leq z \leq 1.06$ (see part I). These materials were prepared by means of a polycondensation reaction between a PEG400/(LiClO₄)_x solution with $0 \leq x \leq 4.890 \cdot 10^{-1}$ and Aluminum isopropoxide. The polymers thus obtained, basically consist of three-dimensional networks with aluminum atoms bridged together by polyetheral chains. Scanning electron microscopy showed a solid-plastic appearance and a smooth texture on the surface of the bulk material. The homogeneity of the systems was confirmed by the absence of microcrystals in the backscattered images. Thermogravimetric investigations indicated that the materials are thermally stable up to ~ 250 °C. Furthermore, a detailed study of the mechanism of ion conduction in these systems was carried out by impedance spectroscopy in the 20 Hz-1MHz range. The analysis of real and imaginary components of conductivity spectra indicated that a full characterization of the AC electrical response for these systems requires an equivalent circuit analysis^[2] for lower frequencies and correlated ionic motion analysis based on the Universal Power Law (UPL)^[3-5] for higher frequencies. The inspection of Nyquist plots (Fig. 1) revealed the presence of semicircular arcs at high frequencies attributed to the bulk properties of the materials; spikes attributed to charge double layer capacities^[6] are present at low frequencies. The dependence of the conductivities on the reciprocal absolute temperature (Fig. 2) present the typical temperature-dependent relation described by the empirical Vogel-Tamman-Fulcher (VTF) equation^[5]. These studies demonstrated that the materials conduct ionically by a mechanism mainly regulated by segmental motion, even if ion hopping between equivalent coordination sites cannot be excluded. The cationic mobility is increased by an unexpeted “anion trapping” ability of the aluminum atoms toward perchlorate anions. Finally, the best conductivity observed in these materials is $1.66 \cdot 10^{-5}$ S·cm⁻¹ at 25 °C. Considering the stability and easy preparation of these hybrid inorganic-organic networks they appear to be profitable for the development of electric energy storage systems.

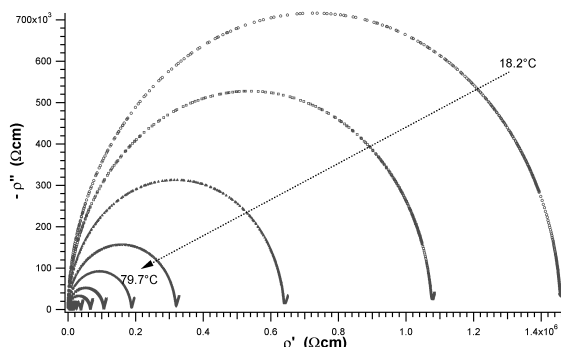


Fig. 1: Nyquist plots of the best aluminum electrolytic complex at various temperatures. The measurements were carried out from 20 Hz to 1 MHz.

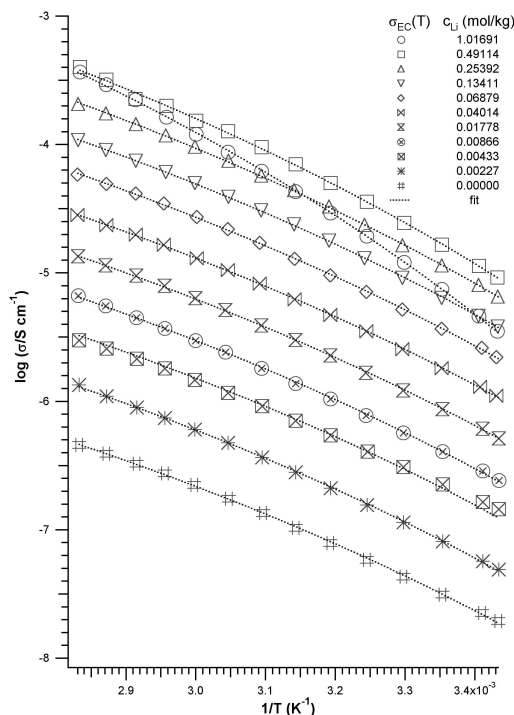


Fig. 2: Dependences of the logarithm of ionic conductivity of the aluminum electrolytic complexes versus the reciprocal temperature. Dotted lines show Vogel-Tamman-Fulcher fitted curves.

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