Peculiarities of ion transport in confined-in-ceramics concentrated polymer electrolytes

R. Blanga[a], M. Berman[b,c], M. Biton[d], F. Tariq[d], V. Yufit[d], A. Gladkich[e], S.G. Greenbaum[b,c], N. Brandon[d], D. Golodnitsky[a,e,*]

[a] School of Chemistry, Tel Aviv University, Israel
[b] Department of Physics and Astronomy, Hunter College of the City University of New York, NY 10065, USA
[c] CUNY Graduate Center, New York, NY 10036, USA
[d] Department of Earth Science and Engineering, Imperial College London, London, UK
[e] Applied Materials Research Center, Tel Aviv University, Tel Aviv 69978, Israel

ABSTRACT

Polyethylene-oxide/lithium-aluminate films were deposited by electrophoretic deposition. Films impregnated with lithium iodide formed highly concentrated polymer-in-ceramic solid electrolytes. Solid-state NMR, FIB-SEM tomography with modelling, and EIS studies showed that only a few percent of the interfacial lithium in the sample is capable of inducing a fast ion-migration path in the system. We suggest that despite suppressed crystallinity of PEO confined in ceramics the ion transport in the polymer medium impedes the total conductivity of the composite electrolyte at near-ambient temperatures. After melting of the polymer and its complexes, the interfacial conduction through perpendicular $LiAlO_2$/LiI grain boundaries becomes feasible. This, together with ion transport via molten, confined polymer electrolyte is followed by the increase of the overall conductivity of the composite system.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The field of solid-state electrochemistry was born in the early 20th century after the recognition by Warburg of the phenomenon of pure ionic conductance in some solid materials [1]. However, rapid progress has only been achieved in the last 30 years by the discovery of solid electrolytes (superionic solids) with high room-temperature conductivity and chemical and electrochemical stability. At present, there is great interest in thin-film lithium-ion-conducting solid electrolytes for application in batteries and hybrid supercapacitors.

The ionic conductivity in solids is caused by the existence of microscopic defects or disorder. Defects include point imperfections in ionic crystals, vacancies, interstitials, antisite and Schottky defects which cause distortion of the lattice in their immediate neighborhood. The structures that permit fast ion transport are generally disordered, channeled or layered [2]. Many of the known superionic solids, such as alkali-metal-conducting beta-alumina, perovskite-type lithium lanthanum titanates, NASICON-type, LiSICON- and thio-LiSICON, garnet-type conducting oxides, LIPON, $Li_{4+x+\delta}(Ge_{1-\delta-x}Ga_x)S_4$, $Li_{10}SnP_2S_{12}$, $Li_7P_2S_8I$ [3–5] are monovalent cationic solids.

Increased room-temperature conductivity of lithium by several orders of magnitude was observed upon replacement of micro-crystalline γ-$LiAlO_2$ with nanocrystalline material [6]. Thin-film ceramic electrolytes are typically produced by vacuum evaporation or sputtering. It has often been observed that they provide different structure, morphology and composition than electrolytes obtained by thermal annealing [2].

Polymer ionics is a relative latecomer to the field of solid-state ionics. Although the complexing ability of oligoethers has been known for some time, Wright and co-workers were the first to measure the ionic conductivity of poly(ethylene oxide) (PEO)- salt complexes [7]. Intensive research has been carried out by Armand et al. and Bruce et al. [8,9]. To date, poly(ethylene oxide)-based polymer electrolytes have been regarded as one of the most suitable electrolytes for lithium batteries. Despite over 30 years of worldwide research on polymer electrolytes (PEs), the requirement of sufficiently high room-temperature cationic conductivity remains inaccessible [9–13]. Furthermore, there is still considerable scientific controversy over the very nature of the ion-transport mechanism and the factors governing cation-anion interactions in polymer-salt complexes based on PEO [10]. Polymer

electrolytes, which usually feature multiphase structures at the microscopic and/or macroscopic levels, make ion transport very complex. First, the coexistence of different phases, such as an amorphous phase and various crystalline complexes of PEO and Li^+, provides different pathways for ion transport; in addition, the distribution and structure of the phases themselves are also intricate. It is established that ion transport in polymer electrolytes includes the local motion of polymer segments and inter- and intra-chain ion-hopping between coordinating oxygen sites, which are not fixed and vary with time and temperature. A number of experimental and theoretical studies of ion transport in polymer electrolytes have resulted in the identification of a variety of relevant transport mechanisms, such as the hopping motion of cations forming a weak coordination shell between Li^+ ions and ether oxygens (EO), free ion motion along percolating channels in the PEO melt, etc. [8–23]. However, among the different controlling factors, the segmental mobility of the polymer backbone has been identified as a key factor in cation and anion mobilities. Hundreds of articles aimed at suppressing the crystallinity of polymer electrolytes have been published and extensive research is still in progress. The research is focused on the synthesis of new block-copolymers, new salts with large anions, plasticizing of polymer matrices by organic and ceramic additives for the improvement of ion conduction that is strongly coupled to the segmental relaxation.

The issue of the effect of ceramic fillers in polymer electrolytes is very important [24] and at present there are several publications that contradict the accumulated knowledge of the composite-polymer field. Many researchers have found that lithium-ion hopping occurs in a sequential manner on the skin areas of ceramic fillers [25–27]. Wieczorek et al. [28] applied the Lewis acid−base theory to explain conductivity enhancement in the case of polymer electrolytes filled with inorganic nanoparticles. In [29] it was found that high-aspect-ratio ceramic nanowires filling a polymer matrix provide long-range Li^+-transfer channels, something not possible in the case of nanoparticles that are randomly distributed in the polymer matrix. Of particular interest are electrolytes which contain high concentrations of ion charge carriers. The main idea of the strategy of polymer-in-salt electrolytes [30–33] is to keep to a minimum the polymer concentration required for good mechanical properties, allowing the major ion-conduction path to go through the inorganic salt. Unfortunately, the cast films are brittle and difficult to handle.

Recently, the simple and inexpensive method of electrophoretic deposition was used by us for the first time to fabricate novel solid ion-conducting polymer-in-ceramic electrolytes [34,35]. EPD provides good conformal deposits on complex and uneven electrode geometries, something particularly important for the elimination of poor point contacts, which cause high internal resistance of the battery. Structure, morphology and ion-conduction properties of composite $LiAlO_2$/PEO films, both pristine and saturated by LiI, have been characterized by a variety of experimental techniques. The choice of the materials is based on the literature data and our previous research. In composite polymer electrolytes, γ-$LiAlO_2$ is combined with polyethylene oxide to improve the mechanical properties, conductivity and the interfacial electrode/electrolyte stability. In [36,37] the authors suggested that nanocrystallites of γ-$LiAlO_2$ [36] and Al_2O_3 in concentrated LiI:PEO electrolytes [37] create highly defective interfacial regions with preferable low-energy conduction paths.

We present here a more detailed study of the ion-conduction mechanism of concentrated confined-in-ceramic $LiAlO_2$/P$(EO)_n$ LiI polymer electrolyte by solid-state NMR, FIB-SEM tomography, and EIS methods. 3D Comsol model, based on FIB-SEM tomography and conductivity data, have been originally applied to the composite polymer-in-ceramic electrolyte system.

2. Experimental

The particle size of the powder in suspension is an important parameter that affects the topography of the deposited films. Micro- and nanosize $LiAlO_2$ particles were used for the deposition of composite films. In order to reduce the size of the particles, wet-milling of 2.0-2.5 μm-size $LiAlO_2$ was carried out in a planetary, high-energy ball mill (PM100 Retsch). 1.0 g $LiAlO_2$, 2.5 ml PEGDME 500 (Merck), 0.5 ml Triton x-100 (Sigma) and 107 g ZrO_2 3mm-Ø balls were introduced into a 50 ml ZrO_2 grinding bowl. The milling was carried out at 450RPM for different periods of time and the sample was transferred to 300 ml ethanol after separation from the balls. The particle-size distribution was measured with a Zetasizer Nano ZS. It was found that the process of wet ball milling markedly reduces the average particle size of $LiAlO_2$ to about 175–190 nm after three hours of milling.

$LiAlO_2$-based composite films were deposited by cathodic EPD, with the use of acetone-based deposition baths of the following composition:250 ml acetone, 0.70–1.84 g $LiAlO_2$ (LAO), 2 ml water, 0.4 ml acetylacetone, 0.027–0.05 g iodine, 0–0.15 g PEI, 0.70 g PEO and 1 ml Triton X-100. A Keithley SourceMeter, model 2400, interfaced with LabTracer software and a PC, were used to control the EPD process and to monitor the current and voltage profiles. Deposition of the membranes was performed on nickel substrates (working electrode) with the use of a graphite plate as counter electrode. The distance between the working and counter electrodes was 1.5 cm. The thickness of the films was about 70–75 μm. Samples for electrochemical-cycling tests were dried under vacuum for 15 hours at 80∘C, and transferred to an argon-filled glove box (Brown, $\leq$10 ppm water) for impregnation with 20%w/w LiI in acetone solution in order to obtain a LiI:P$(EO)_3$ complex and to deposit the excess salt on the ceramic particles. The samples were again dried under vacuum for six hours at 50 °C and transferred to the glove box for cell assembly. Electrochemical-impedance spectroscopy was used to test the conductivity of the composite electrolyte. Conductivity cells (in the coin-cell 2032 setup) comprise the electrolyte sandwiched between two blocking nickel electrodes. Tests were carried out at 25 to 110 °C with a Solartron Impedance Analyzer 1260 at an amplitude of 60 mV and over a frequency range of 15 MHz to 1 Hz.

Surface morphology was tested with a Quanta 200 FEG Environmental Scanning Electron Microscope (ESEM) (JEOL Co.). The ESEM is equipped with an HKL-EBSD and Oxford-EDS integrated analytical system. TOFSIMS tests were performed under the following operating conditions: In^+ primary ions and beam diameter of 1–10 μm with the use of a TRIFT II (Physical Electronics Inc., USA). Wide-line NMR measurements were carried out with a Varian direct-drive 300 MHz spectrometer. A saturated aqueous solution of lithium trifluoromethanesulfonate (lithium triflate) was used as reference, set at 0 ppm for ^{7}Li NMR spectra, which were acquired with the use of a quadrupolar echo sequence. Measurements were carried out at temperatures from 25∘C to 80∘C. ^{7}Li Pulsed Field Gradient NMR (PFGNMR) diffusion measurements were also attempted but were not successful because of very short spin-spin relaxation times. ^{6,7}Li and ^{27}Al Magic-Angle Spinning (MAS) measurements were carried out on a Chemagnetics 3.2 mm MAS probe. Lithium triflate was used as a reference set to 0 ppm for the ^{6,7}Li, while 1 M aqueous $AlCl_3$ was used as a reference set to 0 ppm for the ^{27}Al measurements. Measurements were carried out at 25 °C, 50 °C and 80 °C. Samples were spun at up to 20 kHz. All spectral fits were made with the use of DMFit NMR software.

Three dimensional (3D) imaging of the composite electrolyte was conducted by FIB-SEM tomography, which sections an exposed face of a specimen with a Ga^+ ion beam prior to imaging the face with a high-resolution electron beam. The process is