A Synopsis of Interfacial Phenomena in Lithium-Based Polymer Electrolyte Electrochemical Cells

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Abstract

The interfacial regions between electrode materials, electrolytes and other cell components play key roles in the overall performance of lithium-based batteries. For cell chemistries employing lithium metal, lithium alloy or carbonaceous materials (i.e., lithium-ion cells) as anode materials, a "solid electrolyte interphase" (SEI) layer forms at the anode/electrolyte interface, and the properties of this "passivating" layer significantly affect the practical cell/battery quality and performance. A thin, ionically-conducting SEI on the electrode surface can beneficially reduce or eliminate undesirable side reactions between the electrode and the electrolyte, which can result in a degradation in cell performance. The properties and phenomena attributable to the interfacial regions existing at both anode and cathode surfaces can be characterized to a large extent by electrochemical impedance spectroscopy (EIS) and related techniques.

The intention of the review herewith is to support the future development of lithium-based polymer electrolytes by providing a synopsis of interfacial phenomena that is associated with cell chemistries employing either lithium metal or carbonaceous "composite" electrode structures which are interfaced with polymer electrolytes (i.e., "solvent-free" as well as "plasticized" polymer-binary salt complexes and single ion-conducting polyelectrolytes). Potential approaches to overcoming poor cell performance attributable to interfacial effects are discussed.

Background

The interfacial regions between electroactive materials, electrolytes and other cell components play key roles in the overall performance of lithium-based batteries. For cell chemistries employing lithium metal, lithium alloy or carbonaceous materials (i.e., lithium-ion cells) as anode materials, a "solid electrolyte interphase" (SEI) layer forms at the anode/electrolyte interface, and the properties of this "passivating" layer significantly affect the practical cell/battery quality and performance. Similarly, SEI layers may form at the cathode/electrolyte interface, depending upon the nature of the cathode material. In secondary cells, the SEI layers can influence such characteristics as cell safety, self-discharge, power capability, low-temperature performance, faradaic efficiency, cycle-life and the irreversible capacity loss for the first charge cycle.

For cell chemistries employing organic liquid electrolytes, the technical literature is abundant with studies addressing the SEI formation processes, SEI characterization and the effects of the SEI on cell performance (ref. 1). This is particularly true for chemistries employing lithium metal electrodes, and to a lesser degree "newer" chemistries employing carbonaceous and other lithium ion-intercalating electrode materials. In liquid systems, the SEI composition and morphology is dependent upon both the electrolyte composition (i.e., solvent, salt and

contaminants) as well as the surface properties of the electrode. The often multi-layered SEI is primarily composed of electrolyte decomposition and reduction products, such as inorganic lithium carbonates, oxides and halides, organo-lithium species and often organic polymers.

Their have been relatively few studies of the electrode/electrolyte interface for cell chemistries employing solvent-free solid (SPE) or gelled polymer electrolytes reported in the literature, as these are more newly-emerging technologies compared to liquid electrolyte cell chemistries. It is expected that the passivation phenomena in these systems are similar to those occurring in liquid electrolytes. Most of the polymer electrolyte studies, to date, have focused on polyethylene oxide (PEO)-binary salt electrolytes and PEO-based composite electrolytes containing inorganic/ceramic fillers.

It is assumed that a thermodynamically stable SEI is required at the electrode/polymer electrolyte interface(s) in order to achieve practical performance (e.g., to minimize direct oxidation or reduction reactions between the electrode substrates and the electrolyte and to prevent entry of "solvated" electrons into the electrolyte). The interfaces may have complex morphologies, such as multiple phases or domains, which can lead to uncertainties in elucidating SEI and polymer electrolyte (PE) properties (e.g., ionic diffusion) and in the interpretation of experimental results.

In 2000, the NASA Polymer Energy Rechargeable System (PERS) Program was instituted to support the development of solid polymer electrolytes that exhibit the technical performance necessary for achieving a viable cell/battery to address future aerospace mission needs. The electrolyte performance requirements include: (1) an ionic conductivity of ~10^{-3} S/cm or higher in the desired operational temperature range (e.g., –40 °C to +65 °C), (2) a lithium-ion transport number approaching unity, (3) low interfacial impedance, (4) chemical compatibility with electrode materials, (5) a large window of electrochemical stability, (6) low electronic conductivity, (7) good dimensional and thermal stability and (8) mechanical properties that allow scale-up of the manufacturing process. Electrolyte chemistries and concepts considered included: (1) polymer electrolytes based on "solvent-free" binary salt complexes, (2) cation-conducting polyelectrolytes, (3) polymer-ceramic composites, (4) inorganic-organic hybrids and (5) hybrid/gelled systems.

Depending upon mission requirements and upon technology advancement, advanced lithium-based polymer electrolyte cell/battery chemistries being developed and assessed under the NASA PERS Program may ultimately employ either lithium metal or carbonaceous "composite" electrodes (or alternative advanced electrode materials). Because of the morphology and the rheological properties of polymer electrolytes, wetting and contact problems are to be expected at the electrode/PE interface, and these technical barriers to practical performance (e.g., high internal resistance, low rate capability or insufficient cycle life) must be overcome before the technology can be realistically considered for enhancing or enabling future aerospace missions. "Composite" electrodes may be a cell's performance-limiting component due to their multi-component (e.g., electroactive material, ionically-conducting polymer binder and electronically-conducting filler) and multi-phase composition nature. As supported by extensive experimental data in the literature, the wetting of the individual particles of electroactive material and adequate transport of lithium ions to the particle surfaces will be crucial for the achievement of practical cell/battery performance. Also adding to the complexity of the "composite" electrode structure is the speculation that the polymeric binder phase may not be uniform, but may consist of distinct domains (i.e., "interphases") with different rheological and ionic transport properties.

Experimental

Under the auspices of the NASA PERS Program, Electrochemistry Brach personnel at the NASA Glenn Research Center (GRC) developed experimental methodologies and competencies for characterizing and evaluating polymer-based electrolyte materials and electrolyte-electrode composites. One objective of the PERS Program was to synthesize a variety of "model" electrolyte materials for extensive studies of interfacial behavior; however, viable electrolyte material availability for in-house evaluations was limited. The detailed experimental procedures utilized for in-house studies of electrolyte/electrode interfacial properties were previously reported in the literature (ref. 2). This cited documentation describes the methods for electrode/SPE preparation and electrochemical material characterization testing. Both three-electrode laboratory "Tee" cells and coin cell configurations were employed for both half-cell and full-cell electrochemical evaluations. Charge/discharge cycle testing with Arbin electrochemical instrumentation was used to measure specific capacity and cycling efficiency in electrochemical cell configurations.

Electrochemical impedance spectroscopy (EIS) has been widely used to characterize the nature of lithium-ion electrode processes and interfacial properties, as well as for distinguishing individual contributions to overall cell impedance/resistivity (ref. 3). Impedance data is used to quantify changes that can be linked to electrode film formation and changes in the interfacial properties of the electrode. Also, by comparing impedance spectra at different states of discharge of an electrochemical cell, one can draw rough conclusions about phenomena such as film growth, diffusion resistance, etc. Comparing impedance data as a function of cell cycle life affords a measure of overall cell, as well as individual cell component, stability with time.

Electrochemical impedance data and resulting impedance spectra were obtained using a Solartron 1250 frequency response analyzer coupled to a Solartron 1286 electrochemical interface. The operation of these instruments was automated using Zplot (Scribner Associates, Inc.) software for Windows (Microsoft Corporation). Impedance was measured using a 10 mV signal (55 kHz to 0.1 Hz) with the cell held at its open circuit potential (i.e., the cell is in a state of thermodynamic equilibrium). The sample impedance spectra shown in figure 1 shows features of experimental data that can be interpreted in terms of film resistance, charge transfer resistance and diffusion limitations; these various phenomenological components contributing to the overall cell impedance can be interpreted by fitting the data to an appropriate equivalent electrical circuit model, if desired. The high-frequency intercept (i.e., 628 Ω in the fig. 1 example) corresponds to the bulk resistance (R_b) of the electrolyte and provides a measure of its bulk ionic conductivity.
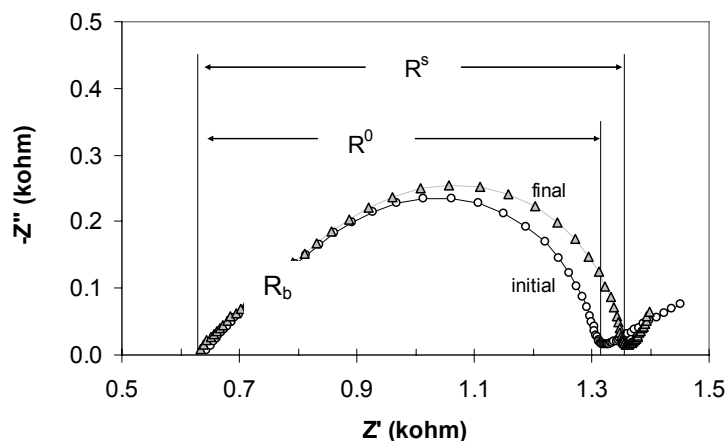

Figure 1.—Electrochemical impedance spectra (Li/SPE/Li cell).

Discussion

The data shown in figure 1 is for a symmetric Li/SPE/Li cell containing a PEO-binary lithium salt complex at 60 °C, and the plot is representative in attributes to most SPE materials that were evaluated at NASA Glenn under the PERS Program. In the figure, R^0 and R^s represent the initial and the steady-state interfacial impedance values, respectively, before and after a 4-hr polarization experiment.

A comparison of the two spectra shown in figure 1 shows an increase in magnitude of a resistive cell component, which is represented by the Z' intercepts of the semicircle, as a result of the cell being polarized. A resultant increase in overall cell resistance occurred, and, as the bulk electrolyte resistance, R_b, remained unchanged during the experiment, this can be attributed to the growth of the resistive interfacial film on either one or both of the electrode surfaces during the polarization. If R^s were to become excessively large in magnitude with time or cycling, the overall cell resistance could become large enough to limit practical cell performance.

In figure 2, the magnitudes of the bulk electrolyte resistances and the interfacial impedances are compared for a Li/SPE/V_6O_{13} cell and a cell with the same electrodes and a standard liquid electrolyte, LP30, prior to cycling. It can clearly be seen that the magnitude of the interfacial impedance, R^0, observed for the complete electrochemical cell is significantly larger for the solid polymer electrolyte cell chemistry, as compared to the liquid electrolyte cell chemistry.

Advanced lithium-based cell chemistries coupled with polymer-based component concepts offer numerous advantages over battery systems employing a liquid electrolyte for future aerospace missions. An all-solid cell design offers inherent safety advantages (e.g., no internal pressure buildup) and affords a reduction in system complexity. If similar cell voltages that are exhibited by lithium-based liquid electrolyte chemistries (e.g., ~4 to 5 V) are achievable, higher energy densities, coupled with lower self-discharge rates, are also projected improvements for solid electrolyte cell concepts; however, most organic polymer electrolytes are not electrochemically stable at such voltages, as the carbon-based polymer structures and/or functional moieties are susceptible to oxidation or reduction. Other variables than cell voltage also contribute to achievable energy density. A flexible shape factor in cell design will enable integration of the energy storage system with structural or other subsystem entities. Also, the exploitation of polymer film-based manufacturing technologies is projected to result in significant production cost reductions.
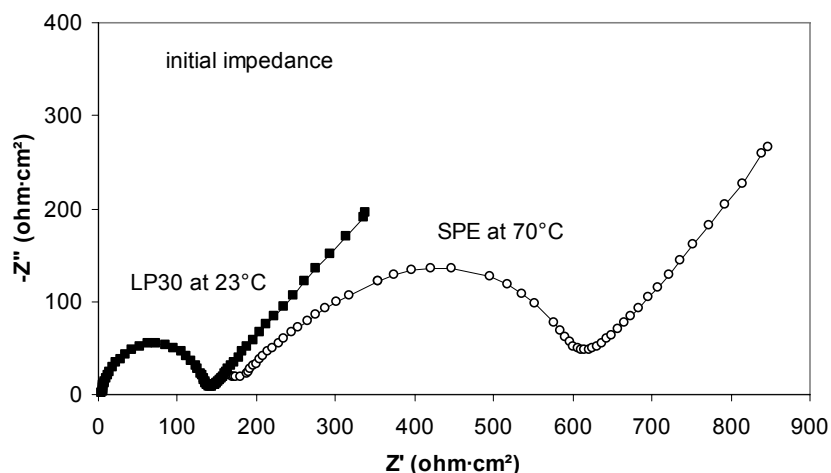

Figure 2.—Comparison of SPE and liquid electrolyte impedance spectra (Li/electrolyte/V_6O_{13} cell).

The following sub-sections summarize interfacial phenomena observed in lithium-based cells with emphasis on cell chemistries employing lithium metal or carbonaceous "composite" electrode structures which are interfaced with polymer electrolytes (i.e., "solvent-free" as well as "plasticized" polymer-binary salt complexes and single ion-conducting polyelectrolytes), as opposed to bulk liquid electrolytes. Potential approaches to overcoming poor cell performance attributable to interfacial effects will also be discussed.

The Nature of the Electrolyte/electrode Interfacial SEI Layer

Whether one considers a liquid, solid polymer or a gel-polymer electrolyte, the nature of the SEI layer/film formed at the electrolyte/electrode interfaces will affect the electrochemical performance of a cell and, perhaps, its practicability. The role of the SEI layer has been the subject of much recent study (ref. 4). The resistive SEI layer must separate the reactive electrode from the electrolyte and must be inert to the electrode itself. The SEI must allow lithium-ion conduction with minimal resistance; it must behave as a single-ion conductor with an ionic conduction mechanism that is different than that occurring in the bulk electrolyte. The SEI must also be mechanically stable to any changes in electrode geometry under different states-of-charge. Basically, the SEI layer properties play a critical role in the satisfactory performance of the electrochemical cell.

The representation of a lithium-polymer cell shown in figure 3 provides insight about the multiple roles that the polymer electrolyte component plays in the cell (ref. 5). In addition to acting as an ionic conductor in the bulk phase, the electrolyte ideally functions as the binder for the electroactive particles in the composite cathode structure and provides a pathway for ionic conduction through the electrode to the particle surfaces. For a dry polymer, segmental motion must be maintained, and for a gel-polymer, solvated ions must travel between the particles. As the presence of solid surfaces can drastically affect polymer dynamics, ionic transport behavior in the composite electrode structure would not be expected to be the same as in the bulk polymer electrolyte (ref. 6).
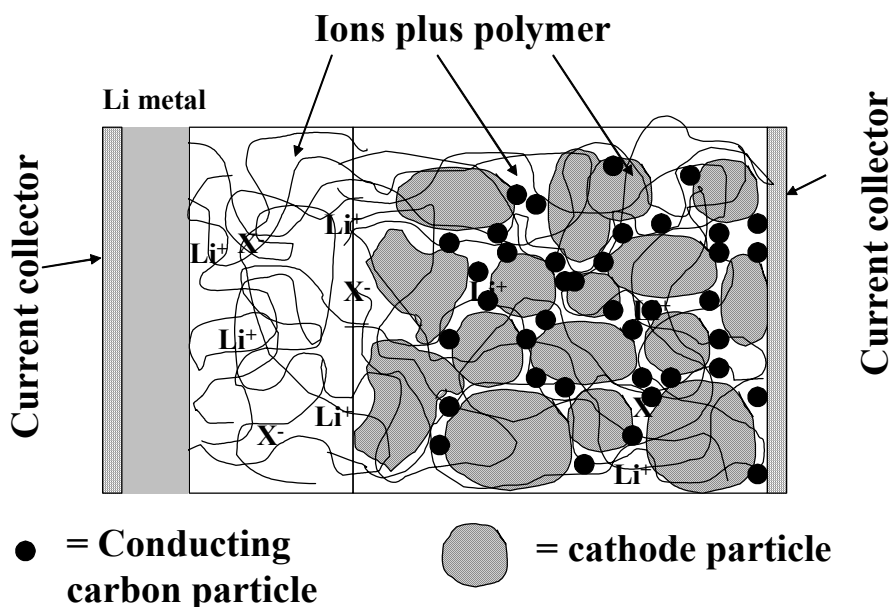

Figure 3.—Representation of a lithium polymer-metal oxide cell (from ref. 5).

The polymer electrolyte's role as a binder and the inherent transport mechanisms described above would be feasible in either a composite cathode or in a composite intercalation anode structure.

As with organic liquid electrolytes, chemical reactions can also occur at the electrolyte/electrode interfaces. At the interface of a metallic lithium anode, carbon-oxygen bond cleavage can be expected, with the formation of alkyl-lithium compounds at the anode surface, which could lead to immobilization of the polymer chain near the surface and, thus, restricted lithium-ion transport through the SEI layer. Besides the polymer, salt anions may also be reactive, and SEI layer formation will occur on the electrode surface. If the SEI formed is thin, robust and a good ionic conductor, it will protect the anode from further undesirable side reactions with the electrolyte. Similar electrolyte side reactions would be expected to occur at cathode surfaces; such reactions could lead to bond formation or cross-linking at the cathode, and thus affect the polymer dynamics close to the cathode surface.

The Metallic Lithium-Polymer Interface

The metallic lithium-polymer electrolyte interface has been extensively studied by EIS, as well as by spectroscopic and microscopic experimental methodologies (refs. 7 and 8). It was found that both impurities in the polymer electrolyte (e.g., stabilizers) and the electrolyte salt and its purity have determining roles in the kinetics of the passivation process and the nature of the SEI layer formed. The low-frequency semicircle in the impedance spectra, as shown in figure 1, was interpreted as a combination of interfacial impedance and charge-transfer impedance. Even though a linear dependence of the current and overvoltage was observed, the electrode process at a polymer/lithium interface could not be necessarily modeled by a simple charge-transfer reaction.

The Carbon Anode-Polymer Interface

The commercialization of lithium-ion batteries was a result of the stabilization of the anode-electrolyte interface in 1990 when Sony announced an anode based on lithium-intercalated carbon or graphite (ref. 9). Lithium-intercalated graphite, LiC_6, is highly reactive towards liquid organic electrolytes, and the by-product of the electrolyte decomposition forms a solid film on the anode surface. Several comprehensive literature reviews of carbonaceous and graphitic anodes (refs. 10 and 11) discuss the effects of the type of carbon on SEI formation, as well as the effects of surface modifications to tailor improved SEI formation. An elucidation of the formation process of an SEI film on graphite during cycling was done by EIS, and it was found that the total film was actually formed through two stages (ref. 12).

The Intercalation Cathode-Polymer Interface

Compounds that are capable of intercalating lithium are of interest as cathode materials because of their reversibility, dimensional stability and absence of co-intercalation of the polymer "solvent". In liquid electrolyte, SEI studies on typical layered metal oxide (Li_xMO_y) cathode materials have shown that cathode-electrolyte interactions result in a surface film that is the source of an observed impedance increase upon cycling. Lithium-ion transport through a SEI layer on cathode material could be rate-limiting, if the surface species are poor ionic conductors and lithium-ion diffusion is fast through the electrolyte and bulk electrode material. The major differences between anode and cathode situations is the more higher first-cycle irreversible capacity observed for an insertion anode, compared to that observed for a typical cathode material (ref. 13).

For polymer electrolyte systems, V_6O_{13} has received considerable attention as a cathode material (ref. 14). EIS studies have been performed to compare capacity performance of pure V_6O_{13} electroactive material with a polymer electrolyte-containing composite cathode material, and an equivalent circuit model for the phenomenological contributions to the observed impedance spectra was rationalized (ref. 15). Results suggested that interfacial impedances arise from reactions with polymer impurities or with the lithium salt rather than the polymer itself. The impedances were found to grow with time until they were larger than the bulk electrolyte impedance.

Polymer Electrolyte Interfacial Behavior

As mentioned previously, the ionic transport process and polymer electrolyte behavior within a SEI layer near an electrode surface, which differ from those within the bulk electrolyte, significantly control the interfacial impedance. This interfacial impedance contributes to the total cell resistance that governs the cell polarization and practical cell efficiency and performance. Insight as to the effects of solid surfaces upon polymer motion and ion transport has been realized from meticulous studies of the effects of ceramic nanoparticle fillers in composite electrolyte systems. Previously reported conductivity enhancements due to such fillers were realized to be due to the scavenging of water and impurities by the fillers, which provided a fast ionic pathway. In actuality, the polymer-surface interaction restricts the polymer segmental motion, and lowered ion mobility is observed in the region of the surface (ref. 16). Thus, the polymer electrolyte surrounding a particle or in direct contact with a surface (e.g., an electroactive material particle or a smooth electrode surface) exhibits different phase properties than the bulk material. Modification of the surface properties can affect the interaction. Molecular dynamic simulation studies have corroborated this influence of solid interfaces on PEO dynamics (ref. 17). These effects also play a role in gel-polymer system dynamics.

Concentration polarization of a cell, which results from salt concentration gradients near the electrode surfaces, can also contribute to voltage losses and poor cell performance, with respect to rate and cycle performance, especially at high current densities (ref. 18). An increase in total cell impedance with cycling can be attributed to the interfacial or charge-transfer impedance. Concentration gradients develop with time because there is only an electrode reaction for the lithium cation and not the anion (ref. 5). The increase in impedance with cycling time for a lithium polymer cell is shown in figure 4.
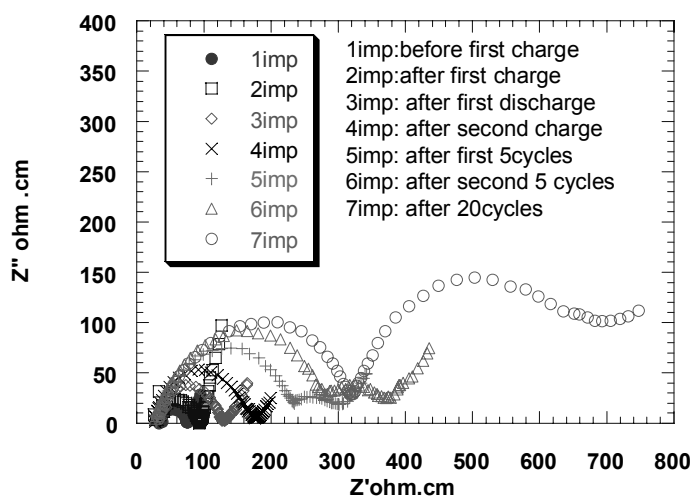

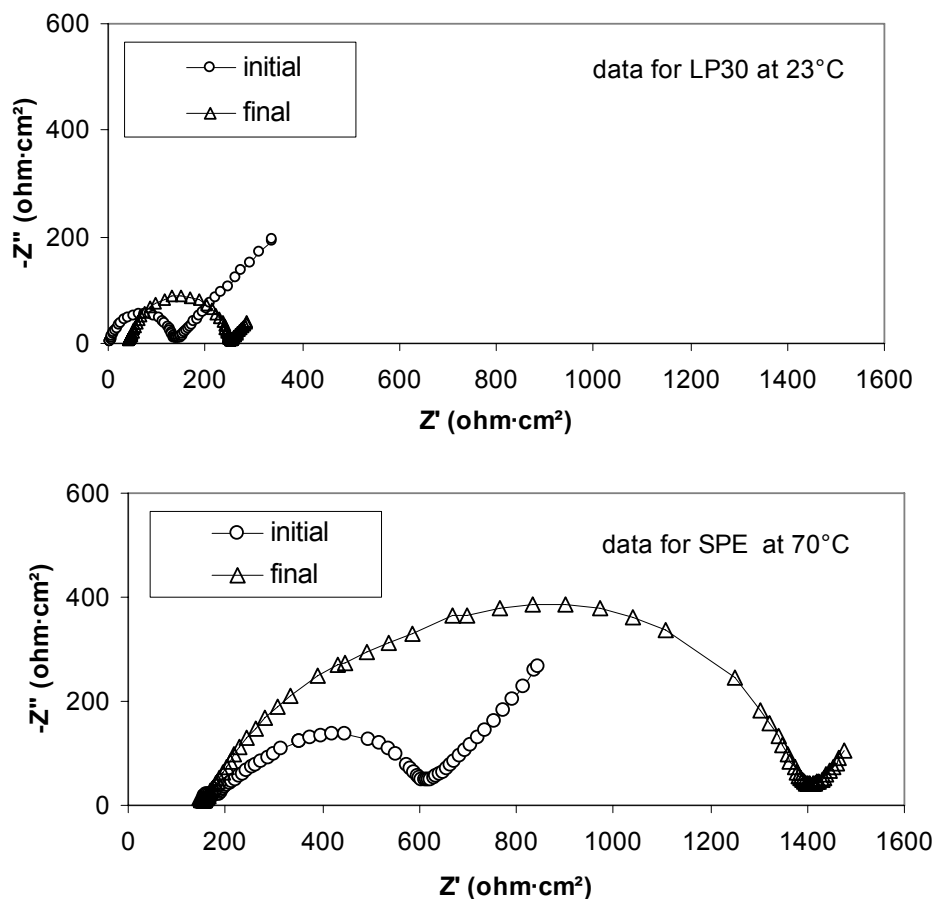Figure 4.—Evolution of cell impedance in a Li/PEO-LiTFSI/V_6O_{13} cell (from ref. 5).

Figure 5.—Evolution of interfacial impedance with cycling (Li/electrolyte/V$_6$O$_{13}$ cell).

The evolution of the interfacial impedance with time was also observed during EIS studies of a polymer-salt complex electrolyte prepared for the PERS Program at NASA GRC. In figure 5, the magnitudes of the increases in interfacial impedance after ~27 charge/discharge cycles are shown for the exploratory SPE material compared to standard LP30 liquid electrolyte.

To experimentally investigate charge-transfer kinetics through the SEI layer, the technique of temperature-step impedance spectroscopy has recently been employed (ref. 19). Measurement of lithium electrode exchange current densities allowed the kinetics at several lithium/polymer interfaces to be characterized over concentration and temperature ranges of practical interest.

Conclusions

Through years of research efforts to develop high-performance, lithium-based batteries containing solvent-free or gelled polymeric electrolytes as viable alternatives to liquid organic electrolytes, it has become well-established that the interactions between the electrolyte and the electroactive material components have a dominant effect on achieving practical performance. The successful development of polymer electrolytes with desired bulk properties is not enough – interfacial properties and interactions and the design of viable "solid electrolyte interphase" (SEI) layers must also be addressed. Interfacial impedances must be minimized in order to achieve

practical cell performance, especially if low-temperature operation is desired. The nature of interfacial processes and phenomena is very complex and dependent upon multiple variables. Surface-polymer interactions were found to significantly influence interfacial polymer dynamics, which govern ionic transport to reaction sites. The successful design of viable polymer electrolytes to overcome practical performance limitations necessitates a comprehensive knowledge of the causes and effects of interfacial phenomena.

Potential approaches to overcoming poor observed cell performance attributed to interfacial effects include modifying the surface properties/chemistry of the electroactive materials, employing electrolyte additives to enhance the interface wetting properties and/or to form a stable SEI, optimizing the "composite" electrode structure with respect to polymer and ionic mobility between the electroactive particles, tailoring the polymer structure to reduce the effects of salt concentration gradients and enhancing polymer dynamics at the interfaces. As an example, a recent approach employing a polymer electrolyte with a novel salt of a weakly-coordinating anion demonstrated an increase in bulk ionic conductivity coupled with a decrease in interfacial impedance (ref. 20). It has also been suggested that as thin-film fabrication technology matures and large surface area materials become viable, this could be a potential alternative approach that would not personify some of the existing interfacial issues.

The complex issue of designing polymer electrolytes for lithium batteries can best be approached with a combination of sophisticated modeling, diagnostic techniques and expanded efforts in material synthesis. System modeling is a viable methodology for defining material property and performance goals, and, thus, could be employed to complement future material development efforts.

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13. SUPPLEMENTARY NOTES

14. ABSTRACT
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