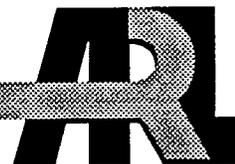


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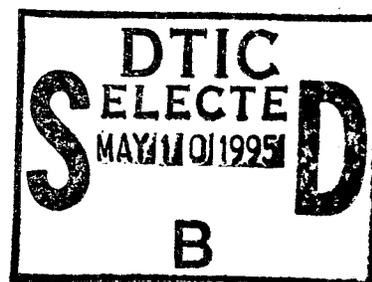


Composite Polymer Electrolyte for Lithium Batteries

Steve Slane and Mark Salomon

ARL-TR-426

March 1995



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13. ABSTRACT (Maximum 200 words) Composite polymer electrolyte films consisting of zeolite powders dispersed in poly-(acrylonitrile)(PAN) based gels with lithium hexafluoroarsenate have been prepared and their electrochemical properties studied. Gel electrolytes prepared by adding lithium hexafluoroarsenate in propylene carbonate (PC) and ethylene carbonate (EC) mixtures with PAN have demonstrated ionic conductivities greater than 0.001 siemens per cm at room temperature and above. The addition of zeolite powders increased ionic conductivity at low temperatures due to the highly amorphous nature of the composite film. Impedance spectroscopy was performed to study the lithium electrode/electrolyte interface, and a reduction of the passivation kinetics was observed. Cyclic voltammetry showed that addition of PAN and zeolite powder to liquid electrolyte mixtures with EC/PC did not change the stable electrochemical potential window. In Li/lithium cobalt dioxide cells, at 25 deg C, these composite electrolytes demonstrated current densities as high as 0.5 milliamps per sq cm, with little voltage or capacity loss compared to cells with liquid electrolytes.			
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Introduction

Polymer gel electrolytes formed by the immobilization of liquid electrolytes in poly(acrylonitrile), (PAN) have ionic conductivities greater than solvent free PEO-based electrolytes [1-3]. There is evidence that the ion transport mechanism for gel electrolytes is more complex than a model of connected liquid electrolyte regions in an inert PAN matrix. Results of nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), and dielectric constant studies [4,5] indicate specific interactions between the electrolyte and PAN. Recently composite electrolytes have been prepared for PEO-based electrolytes with Al_2O_3 [6,7], $\gamma\text{-LiAlO}_2$ [8,9], LiI [7], zeolite type molecular sieves [9], and increased conductivities and decreased Li passivation have been reported. Zeolites have an open three-dimensional framework. They contain water molecules which can undergo reversible dehydration without the framework collapsing. Once dehydrated, the empty cavities will be able to absorb and strongly retain molecules small enough to enter by electrostatic and van der Waals type forces.

For polymer electrolytes to be of practical use, Li-ion mobility must be high enough to enable useful rate capabilities in lithium batteries. For safety, storage, and cycle life the electrolyte must be chemically stable with the electrode materials. In high voltage cells, the electrolyte must also be electrochemically stable over the potential window of the electrode couple. The objective of the present work is to study the electrochemical properties of composite electrolytes in the more conductive PAN-based gels.

Experimental

The preparation of gel electrolyte films involved the immobilization of LiAsF_6 in ethylene carbonate (EC) and propylene carbonate (PC) mixtures with PAN. Composite electrolytes were prepared by the dispersion of ground molecular sieves, sodium aluminosilicates, of the type $\text{Na}_{12}[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}] \cdot 27\text{H}_2\text{O}$ into the mixtures. LiAsF_6 (Lithco "Lectro-salt") was dried under vacuum at 60°C for 24 h. PC (Burdick and Jackson) was dried with type 4A molecular sieves for 48 h then distilled under vacuum. EC (Fluka AG) was fractionated under vacuum. Karl Fisher titration of these solvents indicated water contents of less than 24 ppm. Poly(acrylonitrile) (Polyscience Inc.) with an average molecular weight of 150,000 was dried under vacuum at 60°C for 48 h. Molecular sieves, with effective pore sizes of 4\AA (Davison, Type 4A, 10-16 mesh) and 10\AA (Davison, 13X, 8-12 mesh) were ball-milled for 24 h, dried under vacuum at 200°C for 24 h and sieved to collect powder with a particle size of $\sim 40\ \mu\text{m}$. Smaller particle size (Davison, 13X, powder) with an average particle size of $\sim 2\ \mu\text{m}$ was also studied after drying.

The liquid electrolyte EC:PC: LiAsF_6 was prepared in a 30 ml Pyrex vial with a stirring bar. PAN powder was then added and the mixture stirred to ensure wetting of the PAN. The mixture was heated slowly in an oil bath to $100 - 110^\circ\text{C}$, avoiding overheating and decomposing the PAN. The mixture turned to a clear highly viscous gel and was cast between two glass plates separated with 0.25 mm spacers, and allowed to cool. The resulting polymer electrolyte was an elastomeric mechanically stable film. The film composition, in mole

percent, used in this study was $EC_{40}PC_{34.75}PAN_{21}(LiAsF_6)_{4.25}$. Composite gel films were prepared by adding the ground sieves before heating the mixture as described above. Chemical storage, film casting, and cell assemblies were performed in a Vacuum Atmospheres argon filled dry box.

Electrolyte conductivities and interfacial corrosion were determined from ac impedance measurements using an EG&G Princeton Applied Research (PAR) model 398 impedance system with a frequency range of 5Hz to 1MHz. Conductivity measurements were performed with 316 stainless steel blocking electrodes. A thermocouple was in close proximity to the electrolyte in the cell. The cell assembly was inserted into a wide mouthed glass reaction vessel packed with molecular sieves and then flushed with argon. Measurements were performed in the temperature range of $70^{\circ}C$ to $-70^{\circ}C$ in a Tenney environmental chamber. The corrosion measurements were performed with a Li/electrolyte/Li cell with stainless steel current collectors at $25^{\circ}C$ in an argon filled dry box.

Cyclic voltammetry was performed to determine the electrochemical stability window of the electrolytes using a three electrode cell. The working electrode was platinum, and lithium metal was utilized for both the counter and reference electrodes. Measurements were performed on an EG&G PAR model 273 potentiostat/galvanostat with model 270 electrochemistry software at $25^{\circ}C$.

Composite cathodes were prepared by adding appropriate masses of $LiCoO_2$ (Cyprus) and carbon (Vulcan XC-72) to a gel electrolyte mixture of $EC_{44.3}PC_{39}PAN_{12}(LiAsF_6)_{4.7}$, prepared as above. The powders were added to the gel while hot and mechanically blended in before casting between glass plates. The resulting electrode composition in mass percent was 55/5/40 $LiCoO_2/C$ /polymer electrolyte. Lithium, 1.2 mm, was used as the anode. The cell stack was sandwiched between stainless steel current collectors in a Teflon screw type cell. The working, composite electrode area was approximately 1.0 cm^2 . The cells were cycled with ECO galvanostats between 4.3 and 3.0 volts at $25^{\circ}C$ and the data collected with a Nicolet model 310 digital storage oscilloscope.

Results and discussion

The temperature dependencies of the conductivity of four gel electrolyte films are shown in Fig. 1. Room temperature conductivities were greater than 10^{-3} S cm^{-1} for all four electrolytes studied. A detailed discussion of the ionic conductivity of PAN-based electrolytes has been reported elsewhere [4].

Comparison of composite electrolyte films with an $EC:PC: PAN:LiAsF_6$ film without the addition of zeolites shows an increase in the conductivity at low temperatures. This enhancement in conductivity can be attributed to the preservation of the amorphous phase of the gel films by the dispersion of zeolite particles. The electrolyte films prepared as described have been found to be highly amorphous [2] by x-ray diffraction. At lower temperatures the polymer chain rearranges and aligns in a more ordered or crystalline state, decreasing the

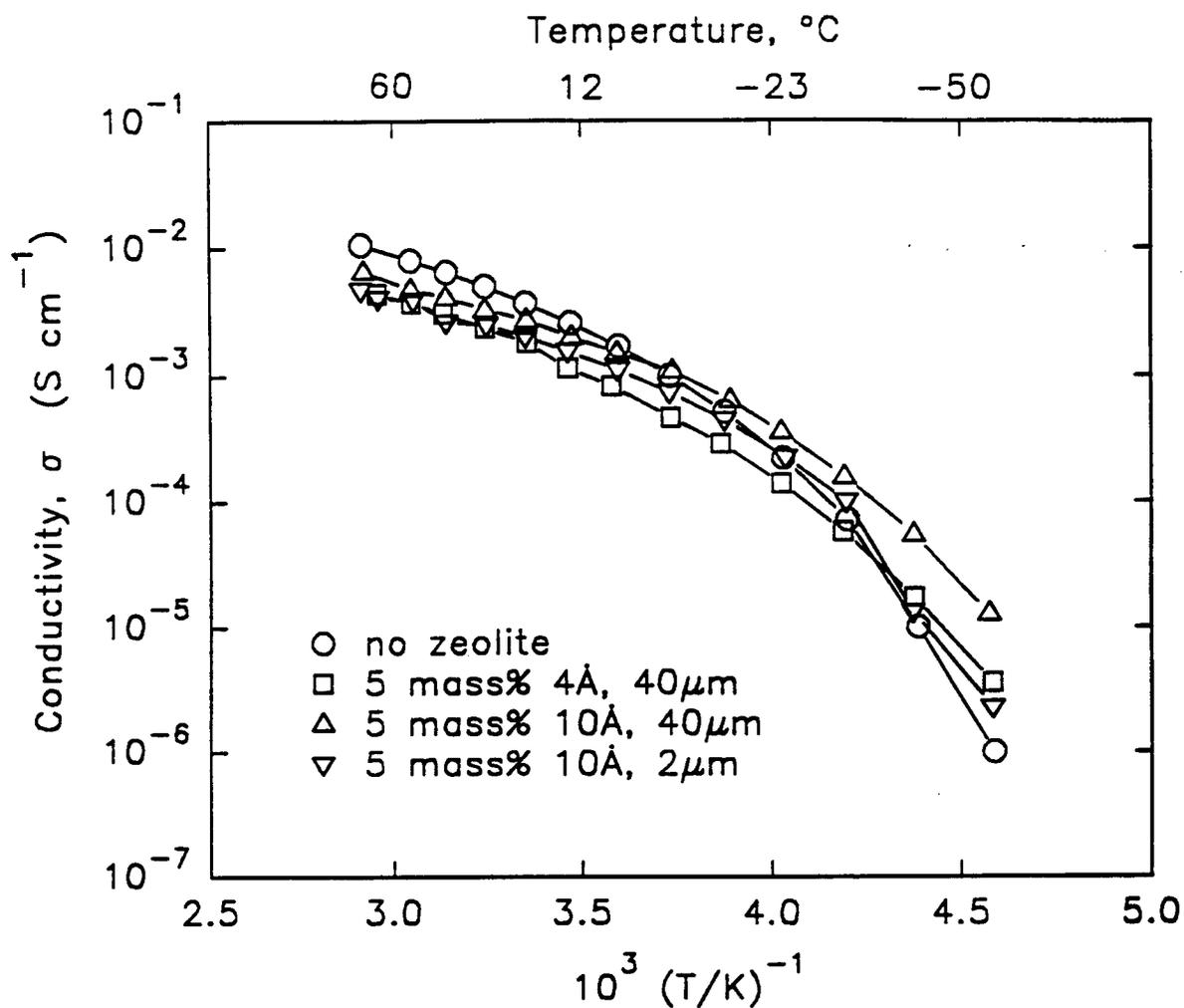


Figure 1. Arrhenius plot of ionic conductivities for composite electrolytes of EC:PC:PAN:LiAsF₆ with zeolite powders.

amorphous regions. Additions of small amounts of zeolite particles dispersed in the electrolyte will prevent this crystallization process. The effect on conductivity due to the amounts of ceramic fillers added to polymer films has been reported to follow a bell-shaped distribution. For the addition of γ -LiAlO₂ to (PEO)₈LiClO₄ the maximum conductivity was measured with 10 mass% of the ceramic filler [8].

To investigate the lithium metal gel electrolyte interface, alternating current impedance spectroscopy was used. The time evolution of the impedance response was monitored for Li/electrolyte/Li cells at open circuit for several weeks. The response, Fig. 2, shows a progressive expansion of the semicircle with time. This semicircle is a measure of the continuous growth of a resistive layer on the Li surface [10], which is the result of corrosion between the Li and the electrolyte. Aprotic solvents such as PC and EC are well known to form passivating layers on Li metal. Growth of these resistive layers will increasingly prevent Li ion transport and thus block the flow of current through the cell. Addition of 5 mass percent zeolite to the gels reduced the rate of growth of the resistive layer on the Li surface. A reduction was found for all the composite films studied. It is believed that this beneficial interfacial characteristic is based, in part, on the water affinity of molecular sieves. The dispersion of ground zeolite traps impurities and prevents them from reacting at the interface. Another possible reason for the improved interface may be due to the composite film being more viscous than the gel electrolytes. This enhanced physical stability may decrease the resistive layer growth by preventing the flow of corrosive solvents to the interface.

The cyclic voltammogram of a composite electrolyte in Fig. 3 indicates a stable electrochemical potential window on Pt of 1V to about 4.4V versus lithium. This voltammogram is typical of liquid LiAsF₆/PC:EC electrolytes and of gel electrolytes based on this chemistry without the addition of zeolite powders. This indicates that PAN and zeolite powders have no effect on the stability window of the electrolyte. The onset potential for lithium deposition on platinum was -0.05V. Lithium stripping is observed by the anodic peak at 0.45V and delithiation of the alloy formed at 0.65V. Sweeps from 3V to 6V, in Fig. 4, show small anodic currents starting at about 4.1V for liquid and gel electrolytes, and smaller currents starting at about 4.3V for the composite electrolyte. This peak is attributed to water oxidation and is further proof that the dispersion of zeolite powders absorbs water molecules in the electrolyte. Higher currents on the order of 1 mA/cm² are observed at 5.3V, due to solvent decomposition. All the reactions described above appear at the same potentials as those reported previously for LiClO₄/PC on a Pt electrode [11].

Utilization of the composite electrolyte in a Li/LiCoO₂ cell is demonstrated by the charge/discharge curves in Fig. 5. The initial cycle is typical of the LiCoO₂ cathode material in liquid organic electrolytes [12]. The cell capacity was 273 mAh per gram of LiCoO₂, and achieved a capacity of 0.5 F/mole on charge at a current density of 0.25 mA/cm² and 0.41 F/mole on discharge at 0.5 mA/cm². After achieving good initial capacity, at what is considered high rates for polymer electrolyte cells, the cell capacity declined steadily and cycling was terminated after 12 charge/discharge cycles.

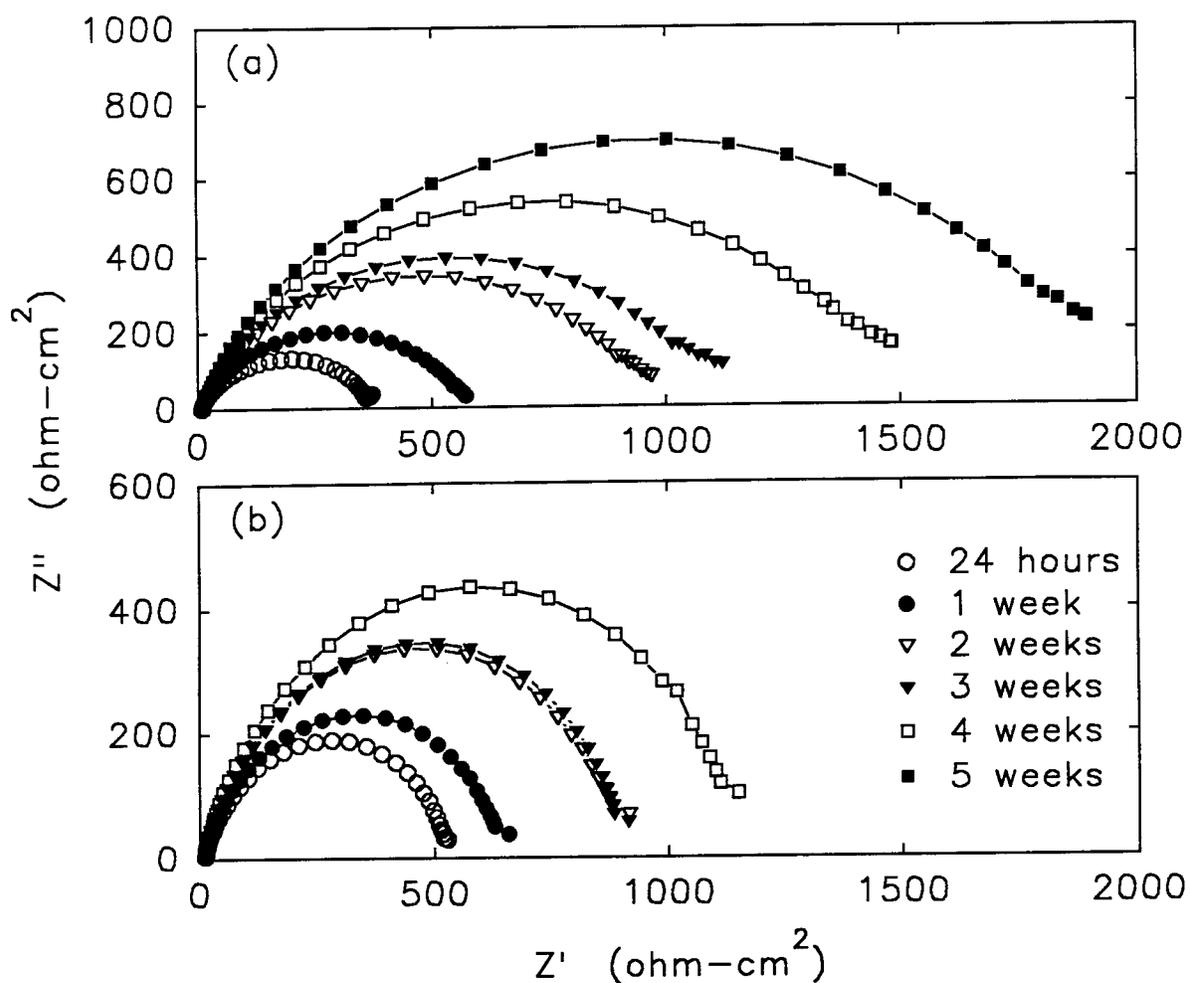


Figure 2. Time evolution of the impedance response of Li/EC:PC: PAN:LiAsF₆/Li cells: (a) gel, (b) composite with 5 mass% 10Å, 40μm zeolite powder.

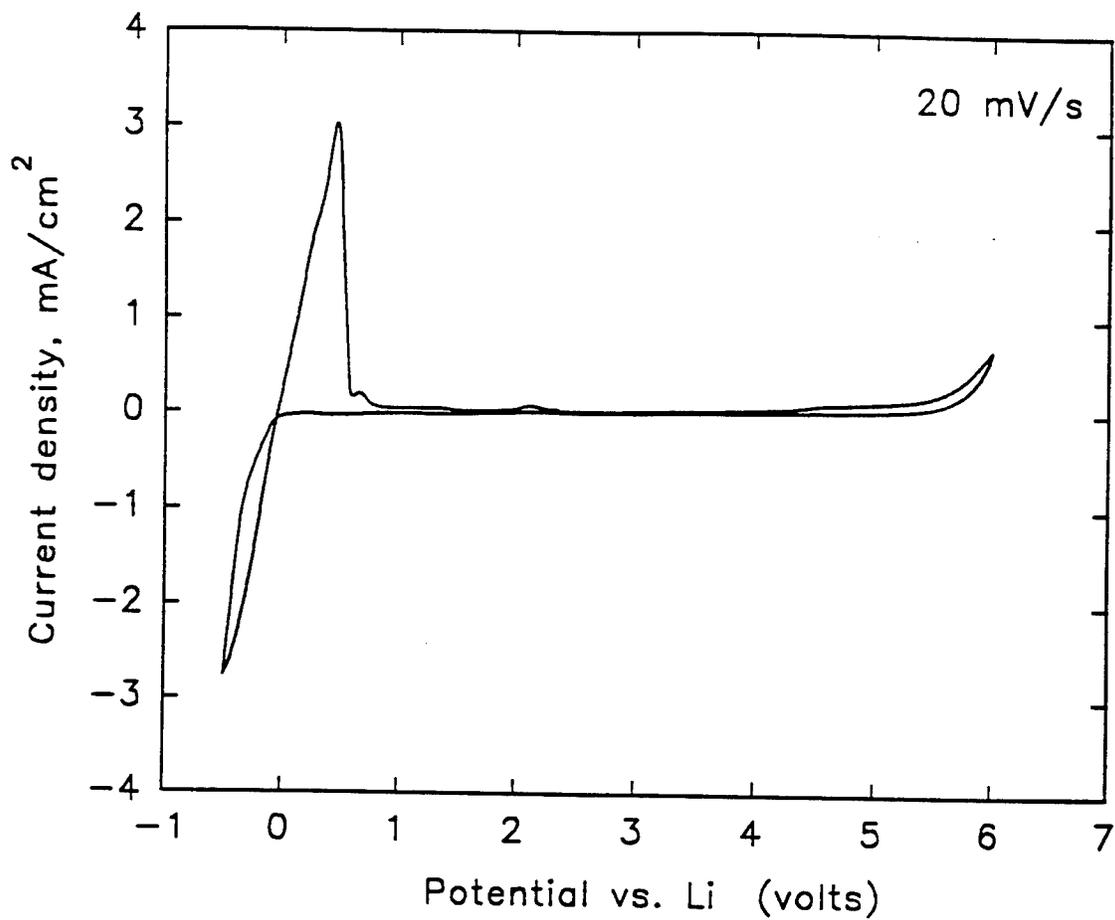


Figure 3. Cyclic voltammogram of EC:PC: PAN:LiAsF₆ composite electrolyte with 5 mass% 10Å, 40μm zeolite powder on a Pt electrode.

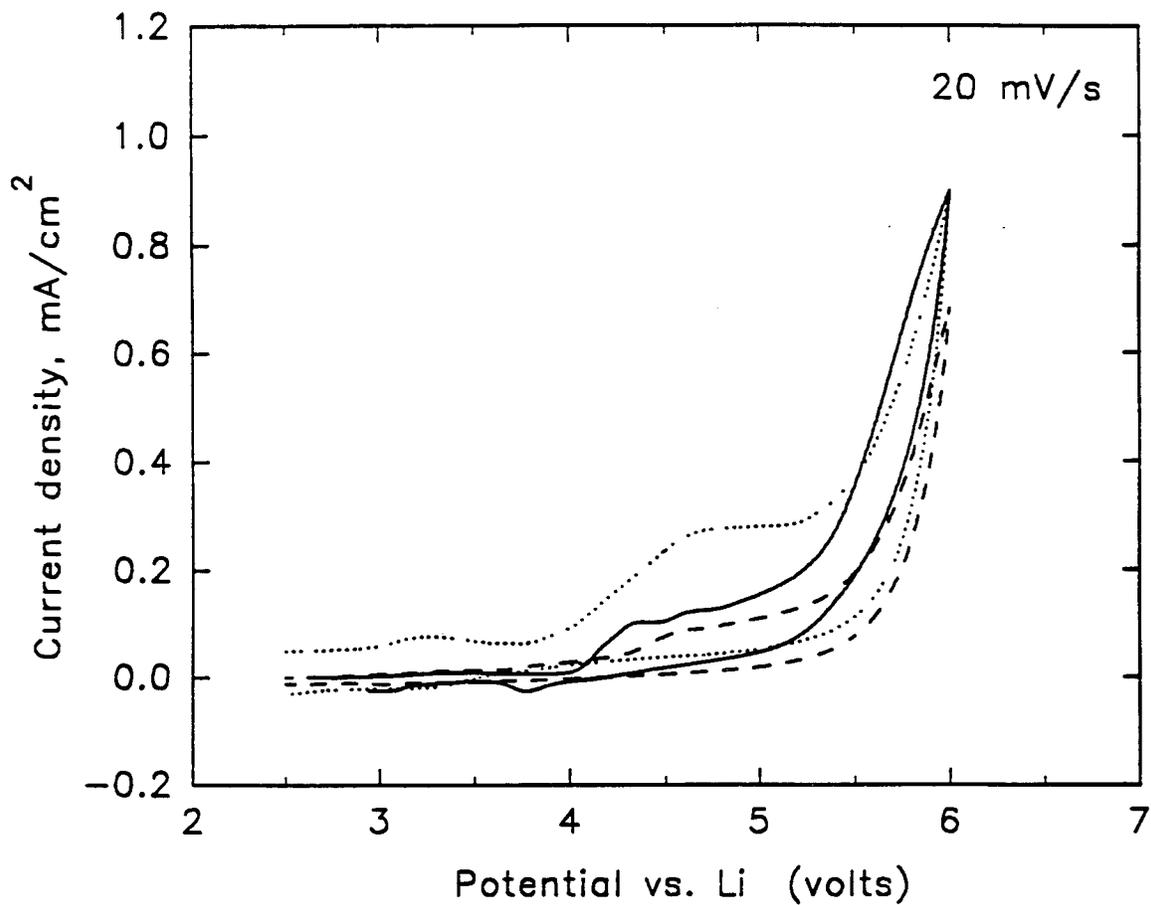


Figure 4. Cyclic voltammogram of (...) 1.4m LiAsF₆/EC:PC liquid, (—) EC:PC: PAN:LiAsF₆ gel and (---) EC:PC: PAN:LiAsF₆ with 5 mass% zeolite composite.

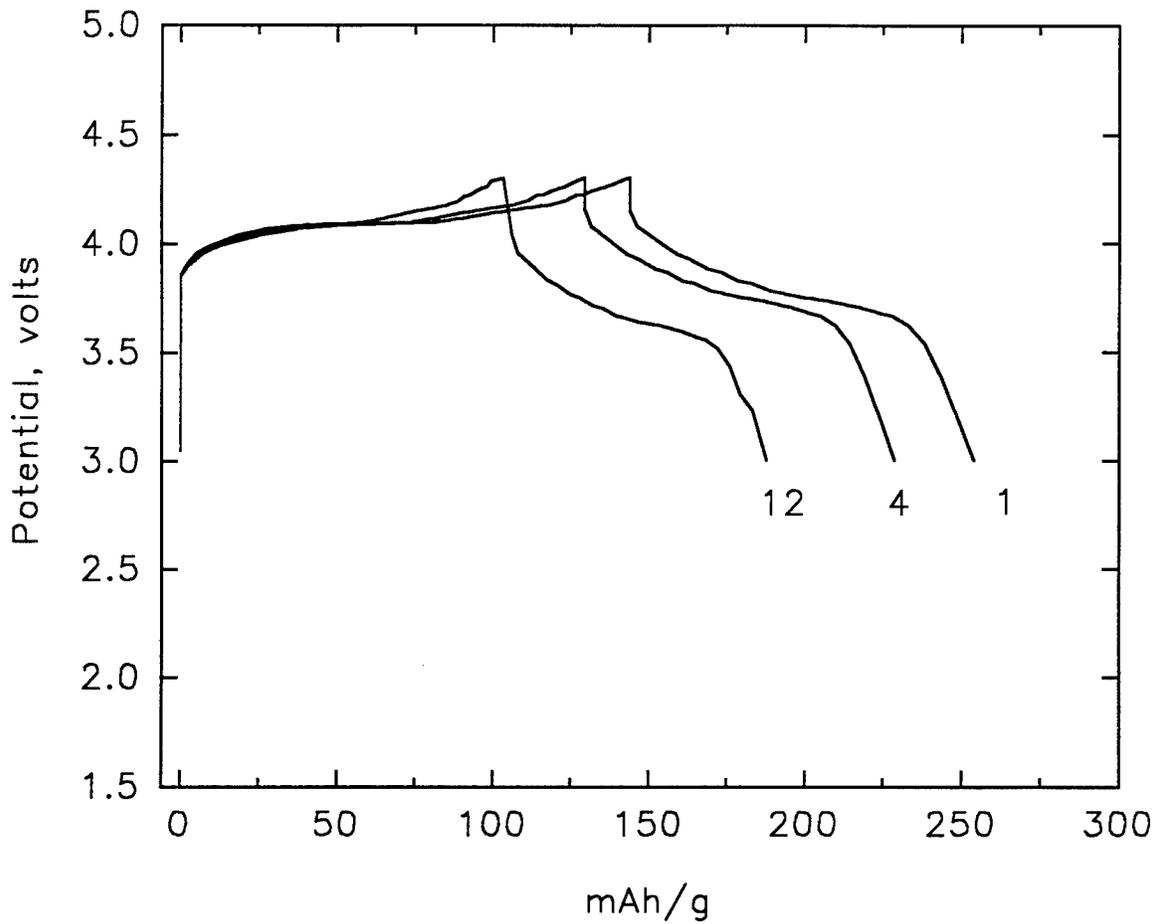


Figure 5. Charge/discharge curves of a Li/LiCoO₂ cell with composite electrolyte EC:PC: PAN:LiAsF₆ and 5 mass% 10Å, 40μm molecular sieves. Charge current density of 0.25 mA/cm² and discharge rate of 0.5 mA/cm².

Conclusions

The results presented above demonstrate that dispersion of powdered molecular sieves in a gel electrolyte increases ionic mobility at lower temperatures and effectively controls the growth of the passivation layer on the lithium electrode. The addition of the ceramic material does not change the stable electrochemical potential window and no significant voltage or capacity loss is observed in a polymer lithium cell.

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