Polyacrylonitrile-based Gelled Electrolytes for Lithium Battery Applications

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Abstract:

A series of polyacr vlonitrilc-based (PAN) electrolytes containing $LiAsF_6$ and' a number of solvent mixtures including Ethylene carbonate (EC) + Propylene carbonate (PC) were prepared and electrochemically evaluated. The typical composition of the electrolyte mixture was PAN -20 MO/O. $LiAsF_6$ -15 MO/O and solvent mixture ~ 6S M%. The highest room temperature lithium ion conductivity measured with these electrolytes was 4.76 x 10^{-3} S/cm. Small capacity (-S mA h) experimental cells with lithium anode and lithium cobalt oxide (Li_xCoO_2) composite cathode and gelled electrolyte of composition (PAN 15 M%; $LiAsF_6$ 10 M% and EC + PC 70 IWO) were fabricated and evaluated for cycle life and cathode utilization efficiency. The cells gave over 2s cycles with a small capacity loss and the cathode utilization efficiency was around 40%.

Introduction:

Gelled polymer electrolytes offer potential possibilities for the realization of lithium polymer batteries for commercial applications. They exhibit very high mom temperature lithium ion conductivity, comparable to that of apr otic solvents, and acceptable mechanical integrity to act as a separator, Mainly, gelled electrolytes have been developed keeping in mind the important properties namely: high lithium ion conductivity (for high rates); structural integrity (to act as a sepal at or) and chemical and electrochemical stability (for long cycle life). Experimental, small capacity, cells with lithium anode and var ious cathodes have been fabricated and evaluated for cycle life and cathode utilization efficiency[1]. For example, Abraham *et al.*[1a] have reported that Li/EC + PC + $LiClO_4$ / TiS_2 (composite cathode) cell could be cycled at high rates with high cathode utilization efficiency (850/0 rrt C/9 rate). We report below our results on the. electrochemical properties of PAN-based gelled electrolytes containing EC + PC + $LiAsF_6$ as well as on the c/d behavior, at room temperature, of Li-$LiCoO_2$ cells containing the above electrolyte.

Experimental:

Electrolyte l'reparation: All the chemicals were used as received with out fur [her purification. Gelled electrolytes with different compositions wer e prepared as given below. Appropriate all) ounts of the components were weighed before hand. Lithium hexafluoro arsenate was dissolved in the solvent mixture and the temper atur c of the liquid electrolyte was raised to 100°C followed by the slow addition of PAN, The temperature was maintained at around 100°C till a clear homogeneous viscous liquid was obtained Thin films were prepared by casting the hot gel between two preheated quartz plates and pressing them together. This procedure yielded thin films with thicknesses -100 µM. We found it necessar y to use polyacrylonitr ile in finely divided powder form to achieve transparent homogeneous clear liquid. Typical composition of the electrolyte was PAN ~20 M%, $LiAsF_6$ -1 S M% and solvent mixture. -65 M%.

Composite Cathode Preparation: Li_xCoO_2 - b a s e d composite cathodes wcr c used for cell studies. Composite cathodes comprises of Li_xCoO_2 (SO w%, acetylene black 10 w% and the polymer electr olyte 40 W%). Polymer electr olyte (same composition as descr ibed in the pr evious section) was prepared beforehand followed by the addition of Li_xCoO_2 and acetylene black, The hot black mixture was uniformly spread on a preheated aluminum foil. The composite electrode was cut to size for later use.

Standard electrochemical equipment were used for the electrochemical evaluation of the gelled electrolyte films and the Arbin cycler was used for c/d studies. The cells were cycled between 4.2 and 3.3 V.

Results and Discussion:

Electrolyte Studies: Electrolytes films were cut to size (- 1 cm^2) and sandwiched between two well polished stainless steel (SS) electrodes (blocking contacts) for both a-c and d c measurements. The a-c measurement was made in the frequency regime 100 kHz to 5117, In Figure 1 is shown the Nyquist plot for the electrolyte of composition PAN -20 M%, $LiAsF_6$ ~15 M% and EC +PC - 65 M%. The x-axis intercept gives the bulk resistance (R_b) of the electrolyte. The resistivity (σ) is 4,76 x 10^{-3} S/cm at room temperature. The near perpendicular plot indicates that there is no measurable charge transfer at the interface. In Figure 2 is shown the d-c voltammetric behavior for the same electr olyte. The electrolyte seems stable in the voltage range 1 to 5 V vs. Li.

Cell St udies: Experimental cells with 1.i anode, $LiCoO_2$ composite cathode (- 4 mAh) and gelled electrolyte were fabricated and cycled at room temperature. Figure 3 provides a plot of capacity vs. cycle #/. The cells were cycled over 25 cycles with a small decline in capacity, Attempts are underway to improve the cathode composition and preparation technique to improve the cathode utilization efficiency and capacity decline.

Conclusions:

PAN-based gelled electr olytes of different compositions were prepar ed and electr ochemically evaluated Among the sever al composit ions studied the electr olyte composition which gave the best conductivit y, of 4.76 x 10-3 S/en) at room temperatur c, was PAN 21 M%; $LiAsF_6$ 8 M% and EC + PC 71 M%. Small capacity experimental cells with $LiCoO_2$ composite cathode were fabricated and tested for cycle life. Although the cells could be cycled over 2S cycles the cathode utilization was poor and the capacity declined with cycling. Impr oved pr eparation techniques will be adopted to minimize capacity decline and increase cathode utilization efficiency.

Acknowledgment:

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References:

1) a) K. M. Abraham and M. Alamgir US Patent # 5,219,679 (1993)
b) K. M Abraham in "Applications of Electroactive Polymers " p 7S edited by B. Scrosati, Chapman & Hall (1993)
c) D. Chua and H-P 1 in US Patent #5,240,790

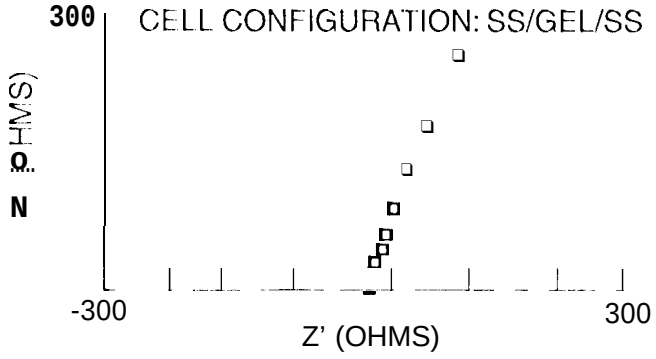

Figure 1, NyQuist plot for the electrolyte containing PAN -20 w??, 1 LiAsF6 --1 S w% and solvent mixture -65 w%.

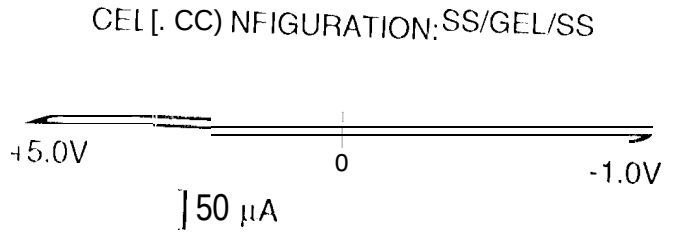

Figure 2. D-C cyclicvoltammetric behavior of the electrolyte (same as in Fig. 1) sandwiched between two well polished stainless steel electrodes.

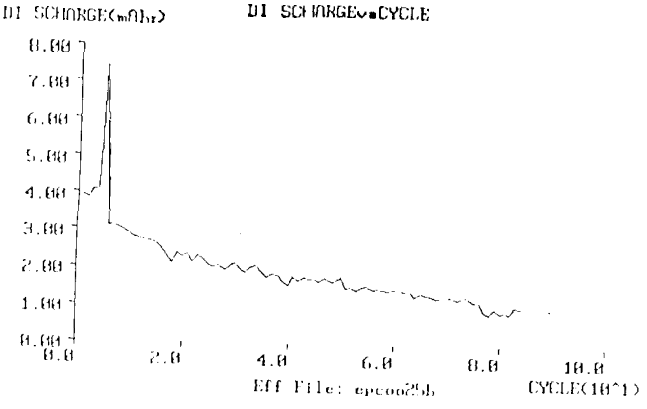

Figure 3. Capacity vs. cycle number for the cell Li/Gelled electrolyte/Composite Li_xCoO_2.* electrolyte same as in Fig 1,