NEW POLYMER ELECTROLYTES BASED ON POLYETHERDIACRYLATES FOR LITHIUM BATTERIES

O.V. Yarmolenko, Yu.V. Baskakova, O.N. Efimov, L.M. Bogdanova, E.A. Dzhavadyan, B.A. Rozenberg

Institute of Problems of Chemical Physics Russian Academy of Sciences, Chernogolovka, Russia

Introduction

Polymer gel electrolytes possessing high ionic conductivity are more advantageous as compared to liquid organic electrolytes used in lithium-polymer batteries now:

- Provided volume equal to that of ion-lithium analog, an electrode surface can be increased and, consequently, current loading and specific capacity can be essentially higher;
- High fire and explosion safety since electrode assembly can be made as a thin monolithic multilayered tape;
- The field of lithium-polymer battery application is very wide ranging from microelectronics to electric engines.

Polymer gel electrolytes [1] comprise an organic electrolyte kept by a swollen polymer matrix and have rubbery consistence. Actually, lithium ions move in a liquid electrolyte kept by a polymer matrix.
We prepared and studied a number of polymer gel electrolytes based on polyacrylonitrile [2] and compositions of oligourethane methacrylate and polypropylene glycol [3]. Here we report on a new generation of electrolytes based on polyesterdiacrylates.

Experimental

Polymer electrolytes were prepared from polyesterdiacrylates of an average molecular weight M_n =1390, which were prepared from the products of anionic polymerization of hydroxyethylacrylate (DAc-OHEA). Oligomer was introduced in an aprotic liquid electrolyte, namely, 1M $LiClO_4$ in γ-butyrolactone and then a film was formed and thermally cured in the presence of a radical initiator, namely, azobis(isobutyronitrile) (2 w/w.%). The film was thermally cured at 80 ^oC for 3 hours.
Electrochemical impedance was measured within 12 - 10^5 Hz range at a measuring signal amplitude equal to 0.005 - 0.01 V using a LCR819 instrument (Goodwill Instruments Ltd.). The experimental data were processed in accordance with the model of adsorption relaxation of a double electrical layer [4]. Symmetrical cells with reversible lithium electrodes were used as electrochemical ones. Glass transition temperature was measured using a DSC 822 differential scanning calorimeter at $5^o.min^{-1}$ scan rate.

Corresponding author:
Yarmolenko O.V.
Tel: (096)5221887, (096)5246777;
e-mail:oyarm@icp.ac.ru, efimov@icp.ac.ru

Results and Discussion

Polymer electrolyte was electrochemically tested depending on a quantity of DAc-OHEA added (Table 1). The impedance spectra of the cells with reversible lithium electrodes are presented in Fig.1. Bulk conductivity of such an electrolyte is usually equal to (2.2÷3.9) . 10^{-3} S.cm^{-1} at 22 °C. Both bulk conductivity and exchange current at an electrode/electrolyte interface are dependent of a quantity of DAc-OHEA added to the system, and exchange current decreases with the diacrylate content increase.

Table 1 *Characteristics of gel electrolyte based on 1M $LiClO_4$/GBL at different content of DAc-OHEA at 22 °C*

Amount of DAc-OHEA (w/w.%)	Glass transition temperature Tg (°C)	Bulk conductivity σ_V (S.cm^{-1})	Exchange current i_0 (A.cm^{-2})
20	-117	$3.9 . 10^{-3}$	$8.6 . 10^{-5}$
25	-112	$2.8 . 10^{-3}$	$6.6 . 10^{-5}$
30	-110	$2.2 . 10^{-3}$	$4.1 . 10^{-5}$

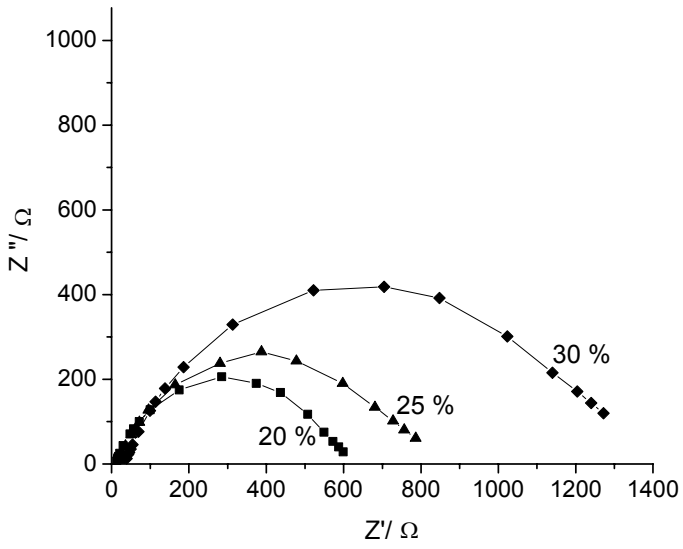

Fig. 1 *Impedance spectra of gel electrolyte based on 1M $LiClO_4$/GBL at different content of DAc-OHEA (w/w.%) in symmetrical Li/Li cell (temperature 22°C, gel thickness is 0.052 cm, electrode surface area is 0.2 cm^2).*

The temperature dependences of electrochemical parameters of the electrolyte were analyzed. The results are summarized in Table 2.

Table 2 *Temperature dependence of electrochemical parameters of gel electrolyte based on 1M $LiClO_4$/GBL and 20 w/w.% of DAc-OHEA*

Temperature (^{0}C)	Bulk conductivity σ_V (S.cm^{-1})	Exchange current I_0 (A.cm^{-2})
-24	$1.2 \cdot 10^{-3}$	$9.3 \cdot 10^{-6}$
0	$1.6 \cdot 10^{-3}$	$2.2 \cdot 10^{-5}$
24	$2.7 \cdot 10^{-3}$	$8.7 \cdot 10^{-5}$

If the temperature changed from -24 ^{o}C up to 24 ^{o}C, bulk conductivity of the electrolyte remained almost unchanged (twice). Exchange currents at the Li/electrolyte interface decreased by an order of magnitude with the temperature varied from 24 ^{o}C down to –24 ^{o}C that is evidence of impeded electron transfer in the reaction: $Li^+ + e \leftrightarrow Li^0$ with the temperature decrease.

Conclusions

Polymer electrolytes based on polyesterdiacrylates prepared from products of anionic polymerization of hydroxyethylacrylate and 80 w/w.% of 1M $LiClO_4$ dissolved in γ-butyrolactone were synthesized and investigated.
Polymer films of plasticized electrolytes have high room-temperature ionic conductivity (up to $3.9 \cdot 10^{-3}$ S.cm^{-1}). Thus, polyesterdiacrylates based on hydroxyethylacrylate can be used for the preparation of plasticized electrolytes for lithium batteries.

Acknowledgements

This work was supported by RFBR (project #03-03-32398), ISTC (project #02-1918), and Department of Chemistry and Materials Science, RAS (project #04-12-131).

References

1. A.M. Skundin, O.N. Efimov, O.V. Yarmolenko, *Russian Advances of Chemistry* **71**, № 4 (2002) 378-398.
2. O.V. Yarmolenko, D.G. Belov, O.N. Efimov: Elektrokhimiya **37** N3 (2001) 321-327 (in Russian).
3. O.V. Yarmolenko, O.N. Efimov, A.V. Kotova, I.A. Matveeva: Elektrokhimiya **39** N5 (2003) 571-577 (in Russian).
4. B.M. Grafov, E.A. Ukshe: Elektrokhimiya **10** (1974) 1875-1882 (in Russian).