New electrolytes and polymer cathode materials for lithium batteries

V. D. Pokhodenko*, V. G. Koshechko and V. A. Krylov

L.V. Pisarzhevsky Institute of Physical Chemistry of the Academy of Sciences of Ukraine, 252028 Kiev, Prospect Nauki 31, (Ukraine)

Abstract

Novel aprotic electrolytes, based on propylene carbonate and γ-butyrolactone compositions with a variety of added organic compounds (polyethers, quinones, aromatic hydrocarbons) have been devised. The electrolytes configured have been shown to be able to form protective, ion-conductive films on the surface of lithium and to improve dramatically the operational characteristics of lithium chemical cells. Processes for synthesizing novel composites, based on conducting organic polymers (polyaniline, polypyrrole, etc.) and transition metal (V_2O_5, TiS_2) binary compounds-challenging cathode materials for secondary lithium batteries have been developed.

Introduction

Recent years have been aggressive interest in lithium batteries on the part of researchers. Such cells, unlike the conventional ones, exhibit much greater magnitudes of electromotive force, energy capacity, shelf and service life [1, 2]. The use of nonaqueous solvents opens up new and wide vistas for creating cells, serviceable at low temperatures.

Researchers' main efforts in upgrading Li batteries are directed at searching for and obtaining new cathode materials that can provide high energy capacity, developing new aprotic electrolyte compositions, improving cell design, solving safety problems, etc. Among these tasks to be tackled the creation of novel electrolyte compositions featuring high conductivity, low viscosity and, good anticorrosive properties as regards the Li anode is most critical. As is known [3–5], the metallic Li–aprotic electrolyte system is thermodynamically unstable as Li reacts with most organic solvents (propylene carbonate (PC), γ-butyrolactone (γ-BL) tetrahydrofuran (THF, etc.). The kinetic stability of a Li anode in such media is associated with formation, on its surface, of a primary protective film incorporating solvent reduction species and a supporting salt. Such a protective ion-conductive film safeguards the surface of the Li anode against corrosion without generally impeding operation of the cell. However, apart from the thin primary film, during protracted storage and maintenance of cells with such electrolytes a thick, loose, secondary film which is a porous polymeric structure resulting from electrolyte destruction species is known [4,5] to form on the Li anode. This contributes, along with other factors, to a marked decline in Li batteries performance and service life. Alternatively, in addition to the organic solvent the Li anode may also react with

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*Author to whom correspondence should be addressed.

diverse impurities adventitiously present in the electrolyte (residual moisture, dissolved O_2, CO_2, etc.).

In view of this one of the promising ways of improving Li cells characteristics and maintaining its stable operation is to search for various additives to the electrolyte, capable of being involved in the formation, on the anode surface, of a stable, ion-conductive film, for staving off the progress of undesirable polymerization processes (secondary passivation film growth, etc.) and for promoting transition of the metallic Li into the electrolyte solution and its implantation into the active cathode material.

Experimental and results

As a result of the investigations carried out in our laboratory it has been demonstrated that a number of organic compounds, notably aromatic polycyclic hydrocarbons (anthracene, phenanthrene, etc.) and crown ethers (dibenzo-18-crown-6, benzo-15-crown-5, etc.) can be used as the additions for electrolytes based on PC or γ-BL. What prompted our selecting the above aromatic hydrocarbons has been the fact that they can react with the metallic Li to form stable anion-radical salts. Such salts can be effective traps for free active radicals resulting from Li-induced destruction of the electrolyte, and can act as inhibitors of free-radical polymerization processes [6]. On the other hand, as is known [6], anion radicals are capable of reacting with proton donor impurities or reactive gases (CO_2, SO_2, O_2, etc.), rendering them inactive:

$$2A^{\cdot} \begin{cases} \xrightarrow{2H^{\oplus}} AH_2 + A \\ \xrightarrow{2CO_2} A(CO_2)_2^{2-} + A \end{cases} \qquad (1)$$

The ability of crown ethers to dissolve almost insoluble Li salts [7] resulting from Li–electrolyte chemical reactions and blocking the anode, cathode and separator predetermines their usefulness as electrolyte-stabilizing dopants. Moreover, owing to complexing, crown ethers bolster enhancement of the electrolyte and passivating film conductivity by taking part in formation of the latter on the Li surface. Also, they can promote increase in the rates of Li electrochemical dissolution and diffusion through the protective film.

The electrolyte compositions incorporating the above additions have been investigated using breadboard models of CR 1/3 N standard-size coil construction cylindrical Li/MnO_2 cells. The additions (0.05–0.5%) have been dissolved in the base electrolyte normally employed in such batteries as propylene carbonate–dimethoxyethane (PC–DME) (1:1) mixture containing 1 M $LiClO_4$.

Injection into the electrolyte of an aromatic hydrocarbon or a crown ether allows, as indicated by our investigations, the discharge capacity and performance efficiency of such cells to be substantially enhanced under conditions of reduced temperatures (-15 °C). As can be seen from Table 1, the above dopants, enable the serviceability of cells under conditions of sufficiently severe pulsed operation at -15 °C to be achieved throughout more than 3000 cycles, whereas with unmodified base electrolyte, given the same conditions, the serviceability of the cells to the test does not exceed 1100 cycles. In addition to the above-mentioned effects, anthracene or dibenzo-18-crown-6, when added to 1 M $LiBF_4$/γ-BL electrolyte, led, as revealed by our experiments run on ML-2325 series cells, to a significant decline (by a factor of 2 to 3) in the growth of the internal resistance of the cells during their storage for two years. The

TABLE 1

Discharge characteristics of the CR 1/3 N-type Li/MnO_2 cell operating on a pulsed basis (pulse mode: 8 s, on, 4 s off; $i = 4$ mA/cm^2). Base electrolyte 1 M $LiClO_4$ in propylene carbonate–dimethoxyethane (1:1) mixture.

Addition to base electrolyte	Discharge capacity, (mA h)		Discharge efficiency (%)		Number of cycles at −15 °C
	20 °C	−15 °C	20 °C	−15 °C	
	190	28.5	75.0	11.4	1100
Anthracene	191	32.0	77.0	15.4	2100
Phenanthrene	191	32.0	77.0	15.4	2000
Dibenzo-18-crown-6	200	58.3	80.0	23.3	3000
18-crown-6	200	55.2	80.0	21.2	3000
Benzo-15-crown-5	200	57.5	80.0	22.4	3000

above additions can therefore inhibit growth of the secondary passivation film on the Li with the lapse of time.

Another line of our efforts has been the search for ways of stabilizing the Li anode through protective coatings created on the surface. A protective film, on one hand, should in a good way safeguard the Li surface against corrosion (reaction with the electrolyte) and on the other have sufficiently high ionic conductivity.

We have ascertained that such a stabilizing effect may be produced by o-quinones. With their high electron affinity o-quinones can react with the metallic Li to form stable anion-radicals.

Lithium anion-radical salts of o-chloramine and o-phenanthrenquinone are poorly soluble in dipolar aprotic solvents and form thin films on the anode surface that avert corrosion of the Li anode and have the necessary ionic conductivity. Injection of o-quinones into the electrolyte based on PC-DME (1:1) and contained within the ML-2325-type button cells, led to an increase in short-circuit current (200 to 350 mA), discharge voltage of the cells on a load of 370 Ω (2.5–3.1 V) as well as in discharge energy which actually rises to the rate value of 120 mA h. The above operating characteristics of the button cells are pretty stable for quite a protracted period of time.

The efforts in upgrading Li chemical cells include, parallel to creation of novel electrolytes, a search for and development of new cathode materials. Speaking of such materials, the attention of researchers has been increasingly focused of late on conducting polymers based on polyaniline, polypyrrole, polythiophene, etc. [8–10]. However, despite important advantages over conventional materials (MnO_2, CuO, TiS_2, etc.) as offered by those their practical development is being restricted so far by a number of problems (high level of self-discharge, low diffusion coefficients, poor stability, etc.) that need to be overcome scientifically yet. Some of the problems mentioned can be partially solved by configuring composites on the basis of organic conducting polymers. Specifically, organic conducting polymers in transition metal oxide intercalation compounds have been prepared recently [11–13]. The composites obtained show some advantage against the precursor materials as the normally nonconducting oxides therein acquire conductivity and the polymers are prone to self-discharge to a much lesser extent.

We have found that emeraldine, polyaniline(PANI)-based form, can be embedded in certain inorganic oxides (V_2O_5, WO_3, Nb_2O_5) to form composites. Notably, the
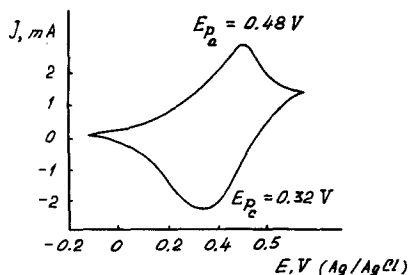
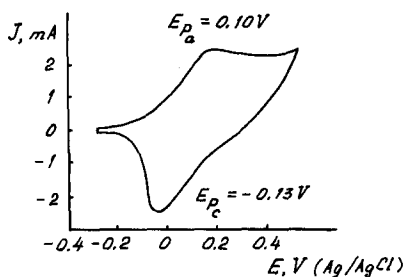Fig. 1. Cyclic voltammogram for $PANI_{0.65}V_2O_5$ composite in 1 M aqueous HCl ($\nu=50$ mV/s).

Fig. 2. Cyclic voltammogram for PP_x-TiS_2 composite in 1 M $LiClO_4/CH_3CN$ ($\nu=50$ mV/s).

resulting $PANI_{0.65}V_2O_5$ composite has been found to be conductive ($\sigma=5\times10^{-2}\ \Omega^{-1}$ cm^{-1}) and paramagnetic. The electron paramagnetic resonance (EPR) spectrum of this compound comprises wide ($g=1.9670$) and narrow ($g=2.0023$) singlet signals attributable to paramagnetic ion V^{4+} and polymeric organic cation radical, respectively. The magnetic resonance and spectroscopy investigations carried out give grounds for believing that $PANI_{0.65}V_2O_5$ is a polymeric organic bronze formed like charge transport implantation compounds [13, 14].

Study of the electrochemical behaviour of $PANI_{0.65}V_2O_5$ has revealed that this material can be subjected to repeated cycling in the range -0.2 to $+1.0$ V without appreciable degradation, the cyclic voltammogram (CV) shows one anodic and one cathodic peak (Fig. 1) which are not recorded by CV for pure PANI and V_2O_5. That there is no apparent degradation of a composite during cycling offers challenges for its application in secondary Li cells.

Conducting-polymer composites can be obtained, as indicated by our investigations, using not only oxides but also sulfides of transition metals, as is the case, for instance, with polypyrrole–TiS_2 composite. Observed in the CV for this material (Fig. 2) is a broad plateau, which may attest to formation of a composite with levelled out attributes of its constituent parts.

At present one of the most routinely-used cathode materials for Li cells is polyfluorinated carbon (CF). This material exhibits low conductivity, poor wettability and compressibility. We have developed CF and polypyrrole(PP)-based plastic composite process. This composite, $PP-(-CF_{0.85}-)_n$, enjoys significantly higher conductivity ($\sigma=3.3\times10^{-2}\ \Omega^{-1}\ cm^{-1}$) than $(-CF_{0.85}-)_n$. Examination of IR spectra for the resulting composite reveals a more ordered, PP-formed structure in the CP matrix, which fact is indicated by the better resolution of the absorption bands and their greater intensity compared with pure PP or a $PP-(-CF_{0.85}-)_n$ mechanical mixture.

Conclusion

Thus, our investigations have yielded several new, modified electrolytes whose application in Li cells enables to improve their operational characteristics markedly and to extend their service life; a new class of composites has been obtained, based on conducting organic polymers with a system of conjugated bonds, which compounds constitute promising cathode materials to be employed in secondary Li cells.

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