Russian Journal of Applied Chemistry, Vol. 76, No. 10, 2003, pp. 1611–1614. Translated from Zhurnal Prikladnoi Khimii, Vol. 76, No. 10, 2003, pp. 1653–1657.
Original Russian Text Copyright © 2003 by Koval', Shembel', Chervakov, Oleinik, Globa.

APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Lithium Salts of *N*,*N*'-Disubstituted Pentanesulfinamidines as Promising Additives for Lithium Power Sources

I. V. Koval', E. M. Shembel', O. V. Chervakov, T. G. Oleinik, and N. I. Globa

Ukrainian State Chemical Engineering University, Dnepropetrovsk, Ukraine
Enerl Inc., Florida, The Unites States

Received May 6, 2003

Abstract—A procedure for preparing new lithium salts with large organic anions, which can be used as additives to nonaqueous electrolytes of high-capacity chemical power sources, was developed. The electrochemical properties of the salts were studied.

Solutions of inorganic lithium salts in pure aprotic solvents or their mixtures are widely used as electrolytes in lithium power sources intended for different purposes.

Recently researchers' efforts have been focused on development of procedures for preparing new, cheap, nontoxic, moisture- and heat-resistant, and chemically and electrochemically stable salts readily soluble in aprotic solvents [1]. This is due to necessity for improvement of the performance of primary and, especially, secondary lithium-metal and lithium-ionic batteries.

The physicochemical properties of lithium organic salts depend on their chemical structure: the nature of the atom to which lithium is bonded and the type of this bond [2]; the nature and size of the anion; the degree of delocalization of the negative charge, which affects the stability of the salt anion [1].

The anion affects the properties of a nonaqueous electrolyte and of lithium power sources for the following reasons. In aprotic solvents, anions are solvated by dipole–dipole interactions which depend on mutual polarization of the anion and the solvent molecules. As the size of the organic anion increases, the polarization becomes stronger, thus enhancing the interaction between the anion and the solvent molecule [3].

Among the known lithium organic salts, lithium salt of bis(trifluoromethanesulfonyl)imide $LiN(SO_2CF_3)_2$ is the most promising as electrolyte for lithium power sources [4–15]. Liquid solutions of this salt have high electrical conductivity and are electrochemically stable up to 4.8 V (relative to lithium reference electrode) [2].

The lithium salt of bis(trifluoromethanesulfonyl)imide and its structural analogues $LiN(SO_2CF_2CF_3)_2$, $LiN(SO_2C_4F_9)_2$, $LiN[(CF_3SO_2)(C_4F_9SO_2)]$ are also used for preparing polymeric electrolytes. The anion size in these lithium organic salts can strongly affect the structural and electrochemical properties of polymeric electrolytes derived from these salts [4].

Lithium salt of bis(trifluoromethanesulfonyl)imide $LiN(SO_2CF_3)_2$ was prepared from bis(trifluoromethanesulfonyl)imide, which is a relatively strong NH acid forming a stable N-anion owing to the presence of two electron-acceptor trifluoromethanesulfonyl groups. Bis(trifluoromethanesulfonyl)imide is not readily available, since substitution of chlorine atoms in the trichloromethyl groups with fluorine [16] requires special equipment and conditions that are difficult to provide in a common chemical laboratory. Alternative components of polymeric electrolytes are lithium salts of aromatic bis(sulfonyl)imides and, in particular, bis(*p*-nitrobenzenesulfonyl)imide $(p\text{-}NO_2C_6H_4SO_2)_2NH$, which is also a relatively strong acid, pK_a 3.2 (aqueous solution) [17].

The structure and acid properties of *N*,*N*'- bisarenesulfonyl substituted imides of iminosulfinic acids are similar to those of aromatic bis(sulfonyl)imides [18]. These compounds inhibit thermooxidative degradation of polymers [19], which is important for electrolytes derived from halogen-containing polymers (polyvinyl chloride, polyvinylidene chloride, polyvinylidene fluoride, etc.).

In this study, we prepared lithium salts of *N,N'*-bis(benzenesulfonyl)pentanesulfinamidine and *N,N'*-bis(*p*-toluenesulfonyl)pentanesulfinamidine and analyzed these salts as additives to liquid and polymeric electrolytes of lithium power sources.

EXPERIMENTAL

N,N'-Bis(benzenesulfonyl)pentanesulfinamidine and its lithium salt were prepared by the following procedures.

***N,N'*-Bis(benzenesulfonyl)pentanesulfinamidine (Ia).** To a solution of dipentyldisulfide (0.001 mol) in acetone (10 ml), sodium salt of *N*-chlorobenzenesulfonamide (0.0042 mol) was added. The mixture was shaken for 30 min, allowed to stand for 12–15 h to negative reaction for available chlorine, and filtered. The solvent was evaporated, and the residue was treated with 10% $NaHCO_3$ (20 ml) and filtered. Compound **Ia** (0.18 g, 43.9%) was isolated from acidified filtrate. The product was identified by melting point (mixing with an authentic sample) and by IR spectroscopy.

Compound **Ib** was prepared similarly in 45.4% yield.

Lithium salt of *N,N'*-bis(benzenesulfonyl)pentanesulfinamidine (IIa). To a solution of **Ia** (0.001 mol) in acetone (10 ml), equimolar amount of LiOH dissolved in a minimal volume of methanol or water was added. The reaction mixture was shaken for several minutes and filtered. The solvent was removed in air. The residue was dried to constant weight in a desiccator over $CaCl_2$. Compound **IIa** was obtained in the form of a colorless powder decomposing at 88–90°C.

Found (%): N 6.34

$C_{17}H_{21}N_2O_4S_3Li$.

Calculated (%): N 6.66.

Salt **IIb** was prepared similarly in quantitative yield in the form of a colorless powder decomposing at 147–150°C.

Found (%): N 6.12

$C_{19}H_{25}N_2O_4S_3Li$.

Calculated (%): N 6.25.

The IR spectra (KBr pellets) were recorded on a UR-20 spectrophotometer.

The dissociation constant pK_a of **IIa** in a 1% methanol solution was determined by potentiometric titration at 24 ± 2°C on a pH-121 millivoltmeter with an automated titration unit. Glass ESP/41-G-04 electrode served as working electrode, and a silver chloride electrode, as reference electrode. A 0.1 M solution of **Ia** was titrated with 0.1 M KOH.

The electrical conductivity of these salts in nonaqueous electrolytes was measured and the range of electrochemical stability of these solutions was determined. The behavior of the modified electrolytes in model secondary lithium power sources Li–MnO_2 and Li–V_6O_{13} was studied.

The electrical conductivity of solution of the lithium salts in aprotic organic solvents was measured by impedance spectroscopy in a temperature-controlled glass electrochemical cell with parallel platinum electrodes. The measurements were performed at a working frequency of 80 kHz and temperature of 24 ± 2°C. The electrolyte conductivity χ (S cm^{-1}) was calculated by the equation

$$\chi = KG,$$

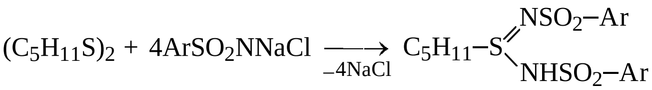
where G is the conductance of the electrolyte in the cell (S), and K is the cell constant determined using 0.01 M aqueous solution of KCl (cm^{-1}).

The range of electrochemical stability of the lithium salts was determined by cyclic voltammetry under potentiodynamic conditions. The experiment was performed under an argon atmosphere in a three-electrode Teflon cell of disc design, containing working, reference, and auxiliary electrodes. The reference and auxiliary electrodes were made of metallic lithium. A platinum plate with surface area of 8.0×10^{-3} cm^2 was used as working electrode. The electrode potential was set with a PI-50-1.1 potentiostat and a PR-8 programmer. The sweep rate was 20 mV s^{-1}. The cyclovoltammograms were recorded on a PDA-1 *XY*-recorder in the potential range from 1.1 to 4.6 V.

Polymeric electrolytes (PEs) were prepared on glass supports from THF solutions containing a polymer, lithium salt, and additive (synthesized lithium salt with organic cation). The PE films were dried for 24 h at room temperature and for 48 h in a vacuum at 45°C.

Charging–discharge cycling of the model lithium power sources with polymeric electrolytes containing the synthesized lithium organic salts was performed in the geometry of 2325 disc battery. The electrode structure was obtained by layer-by-layer application of the polymeric electrolyte between lithium anode and cathode. The thickness of the polymeric electrolyte and the lithium anode was 0.03 and 0.8 mm, respectively. The cathode was prepared from a mixture of chemically synthesized MnO_2 or V_6O_{13} (80 wt %), carbon (5 wt %), graphite (5 wt %), and F-4D fluoroplastic binder (10 wt %).

N,*N*'-Bis(benzenesulfonyl)pentanesulfinamidines were obtained using the known modified procedure [20]. Dipentyl disulfide was oxidatively iminated with sodium *N*-chloroarenesulfonamide in acetone by the reaction

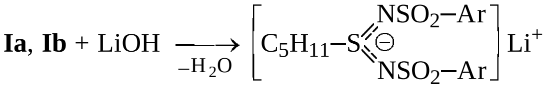


$$(C_5H_{11}S)_2 + 4ArSO_2NNaCl \xrightarrow[-4NaCl]{} C_5H_{11}{-}S\begin{array}{l}{=}NSO_2{-}Ar\\ {-}NHSO_2{-}Ar\end{array}$$

Ia, **Ib**

Compounds **Ia** and **Ib** were indetified by melting points (mixing with known samples), by determining the neutralization equivalent, and by IR spectroscopy. These compounds are relatively strong NH acids (pK_a of **Ia** is 2.91), which can be titrated with an alkali in alcoholic solution in the presence of Methyl Red as indicator. The equivalent weight determined by titration agrees with the calculated data. The IR spectra of Ia and Ib contain the bands of stretching vibrations of the SO_2 (1160–1158 and 1310–1335 cm^{-1}) S=N (753–765 cm^{-1}), CH_3 (2925–2950 cm^{-1}), CH_2 (2841–2850 cm^{-1}), and CH (ar.) (1485–1533 cm^{-1}) groups. Two strong bands in the range 3250–3360 cm^{-1} are assigned to N–H stretching vibrations. This type of absorption by the N–H bonds is due to prototropic tautomerism in the N–S–N triad, which has been found previously in *N*,*N*'-bis(arenesulfonyl)sulfinamidines [18].

The lithium salts were prepared by neutralization of appropriate pentanesulfinamidines with equimolar amounts of LiOH in acetone–methanol–water mixture [21]:



$$\mathbf{Ia}, \mathbf{Ib} + LiOH \xrightarrow[-H_2O]{} \left[C_5H_{11}{-}S^{\ominus}\begin{array}{l}{=}NSO_2{-}Ar\\ {=}NSO_2{-}Ar\end{array}\right]Li^+$$

IIa, **IIb**

where Ar = Ph (**a**), *p*-MeC_6H_4 (**b**).

The solvents were evaporated in air, and the residue was dried in a desiccator over $CaCl_2$. **IIa** and **IIb** were obtained in the form of colorless hygroscopic powders or oily substances decomposing in a wide temperature range.

The composition and structure of salts **IIa** and **IIb** was confirmed by elemental analysis and IR spectroscopy. The IR spectra of these compounds contain the bands of stretching vibrations of the SO_2 (1160–1165 and 1310–1330 cm^{-1}) and S=N (1030–1040 cm^{-1}) groups and bands of other groups. The NH bands are absent.

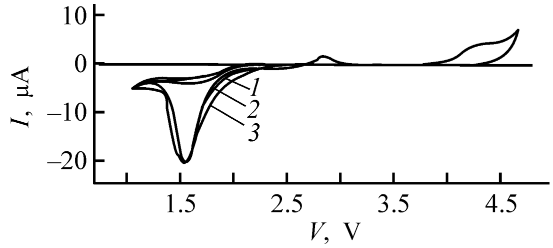


Fig. 1. Cyclic voltammogram of 0.5 M solution of lithium salt **IIa** in PC. Sweep rate 20 mV s^{-1} (*I*) Current and (*V*) voltage.

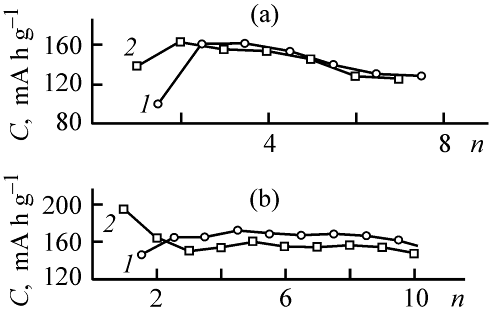


Fig. 2. Specific capacity *C* of Li/PE/MnO_2 system in a 2325 battery vs. the number of charging–discharge cycles. PE composition: (a) c-PVC : PC : $LiCF_3SO_3$ = 19.2 : 75.1 : 5.7 and (b) c-PVC : PC : $LiCF_3SO_3$: **IIa** = 18.1 : 72.5 : 3.1 : 6.3. (*n*) Cycle no. $I_{charge} = I_{discharge}$ = 100 μA.

Salts **IIa** and **IIb** are readily soluble in aprotic solvents.

The conductivity of a 0.24 M solution of **IIa** in dimethylformamide and 0.5 M solution of **IIb** in propylene carbonate (PC) is 6.0×10^{-3} and 5.2×10^{-4} S cm^{-1}, respectively.

Cyclic voltammograms of a 0.5 M solution of **IIa** in PC, recorded on a platinum electrode under potentiodynamic conditions, are shown in Fig. 1. As seen from Fig. 1, this compound is stable under conditions of repeated potential sweeping in the range 1.1–4.6 V.

Since this additive is electrochemically stable in a wide potential range, it can be used in lithium power sources with different discharge voltages: 3.8 (lithium–ionic systems), 2.8 (lithium–metal secondary systems with oxide cathode), and 1.8 V (lithium–metallic systems with sulfide cathode).

We used salt **IIa** as a modifying additive to PE based on chlorinated polyvinyl chloride (c-PVC) or vinylidene fluoride–hexafluoropropylene copolymer.

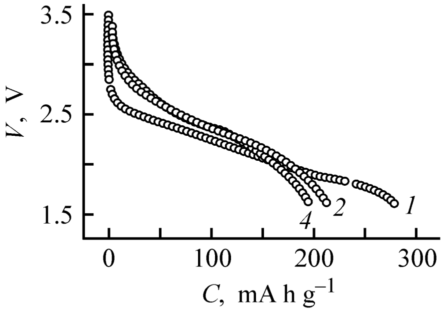


Fig. 3. Discharge curve of the Li/PE/V_6O_{13} system. Polymeric electrolyte based on microporous vinylidene fluoride–hexafluoropropylene copolymer modified with lithium salt **IIa**. $I_{\text{charge}} = 120$, $I_{\text{discharge}} = 290$ μA. (*V*) Voltage, and (*C*) specific capacity. *Digits at the curves* correspond to the cycle numbers.

Power sources with plasticized and microporous PEs modified with lithium salt of *N,N'*-bis(benzenesulfonyl)pentanesulfinamidine **IIa** have good charging–discharge parameters and are stable under conditions of repeated cycling of the Li–MnO_2 (Figs. 2a, 2b) and Li–V_6O_{13} (Fig. 3) systems. It should be noted that addition of **IIa** makes longer the shelf life of the Li-V_6O_{13} system. The discharge curves of a model lithium power source with a V_6O_{13} cathode, stored for 1 month, are shown in Fig. 3.

CONCLUSIONS

(1) Lithium salts of *N,N'*-bis(benzenesulfonyl)pentanesulfinamidine and *N,N'*-bis(*p*-tolyenesulfonyl) pentanesulfinamidine were synthesized.

(2) The electrical conductivity of nonaqueous solutions of these salts is relatively high even at low salt concentration . The conductivity of a 0.24 M solution of **IIa** in dimethylformamide and 0.5 M solution of **IIb** in propylene carbonate is 6.0×10^{-3} and 5.2×10^{-4} S cm^{-1}, respectively.

(3) Solutions of the lithium salts in propylene carbonate are electrochemically stable at potentials of 1.1 to 4.6 V relative to lithium reference electrode.

(4) The lithium salt of *N,N'*-disubstitued pentanesulfinamidine can be used as additive to polymeric electrolytes to stabilize the discharge properties and decrease the self-discharge of lithium power sources.

ACKNOWLEDGMENTS

The authors are grateful to O.V. Kolomoets and I.M. Maksyuta for studying the conductivity and electrochemical stability of the electrolytes.

REFERENCES

1. Barthel, J., Buestrich, R., Gores, H.J., *et al.*, *J. Electrochem. Soc.*, 1997, vol. 144, no. 11, pp. 3866–3870.
2. Kita, F. Sakata, H., Kawakami, A., *et al.*, Abstracts of Papers, *1999 Joint Int. Meet.*, Honolulu, Hawaii, October 17–22, 1999, abstract no. 341.
3. Parker, A.J., *Usp. Khim.*, 1963, vol. 32, no. 10, pp. 1270–1295.
4. Passerini, S., Appetecchi, G.B., Villano, P., *et al.*, Abstrcats of Papers, *2001 Joint Int. Meet.*, San Francisco (USA), September 2–7, 2001, abstract no. 94.
5. Saito, Y., Capiglia, C., Yamamoto, H., and Mastarelli, P., *J. Electrochem. Soc.*, 2000, vol. 145, no. 5, pp. 1645–1650.
6. Krause, L.I., Lamanna, W., Summerfield, J., *et al.*, *J. Power Sources*, 1997, vol. 68, pp. 320–324.
7. Abraham, K.M. and Jiang, Z., *J. Electrochem. Soc.*, 1997, vol. 144, no. 6, pp. L136–L138.
8. Xia, Y., Tatsumi, K., Fujieda, T., *et al.*, *J. Electrochem. Soc.*, 2000, vol. 147, no. 6, pp. 2050–2056.
9. Yamada, O., Ishikawa, M., and Morita, M., *Electrochim. Acta*, 2000, vol. 45, pp. 2197–2201.
10. Aihara, Y., Hayamizu, K., Sugimoto, K., *et al.*, *J. Power Sources*, 2001, vols. 97–98, pp. 628–631.
11. Itoh, T., Hirata, N., Wen, Z., *et al.*, *J. Power Sources*, 2001, vols. 97–98, pp. 637–640.
12. Li, Q., Takeda, Y., Imanish, N., *et al.*, *J. Power Sources*, 2001, vols. 97–98, pp. 795–797.
13. Matsuda, Y. and Takenutsu, T., Abstract of Papers, *10 Int. Meet. on Lithium Batteries*, Como (Italy), May 28–June 2, 2000, abstract no. 288.
14. Lee, W.C., Joachin, H.J., and Prakash, J., Abstracts of Papers, *198th Meet. of the Electrochemical Society*, Phoenix (USA), October 22–27, 2000, abstract no. 143.
15. Ogumi, Z., Ohkubo, T., Abe, T., *et al.*, Abstracts of Papers, *198th Meeting of the Electrochemical Society*, Phoenix (USA), October 22–27, 2000, abstract no. 159.
16. Koval’, I.V., *Usp. Khim.*, 1991, vol. 60, no. 8, pp. 1645–1679.
17. Reibel, L. Bayound, S., Baudri, P., and Majastre, H., *Electrochim. Acta*, 1998, vol. 43, nos. 10–11, pp. 1171–1176
18. Koval’, I.V., *Sulfur Rep.*, 1993, vol. 14, pp. 149–221.
19. Koval’, I.V., Oleinik, T.G., Basanets, K.S., *et al.*, Abstracts of Papers, *Nauchno-teknicheskaya konferentsiya “Perspektivy razvitiya promyshlennosti plastmass v Ukraine”* (Scientific and Technical Conf. “Prospects of Development of Plastic Production Industry in Ukraine”), Lviv, September 12–17, 1995, p. 63.
20. Koval’, I.V., Tarasenko, A.I., and Kremlev, M.M., *Zh. Org. Khim.*, 1986, vol. 22, no. 2, pp. 410–415.
21. US Patent Appl. 10/122,788.