Effect of physicochemical properties of electrolyte systems on behavior of lithium sulfur cells

Kolosnitsyn V.S., Kuzmina E.V., Karaseva E.V., Sheina L.V. Institution of the Russian Academy of Sciences Institute of Organic Chemistry of Ufa Scientific Centre of the Russian Academy of Sciences 71, pr. Oktyabrya, Ufa, Bashkortostan, 450054, Russia e-mail: <u>kolos@anrb.ru</u>, <u>kuzmina@anrb.ru</u>

The lithium sulfur batteries are chemical power sources with liquid cathodes [1]. Therefore it should be expected that their electrochemical properties would significantly depend on physicochemical properties of electrolyte system.

The aim of this work was investigation of effect of physicochemical properties of lithium salt solution in sulfolane on some regularity of cycling of lithium-sulfur cells.

The investigations were made in Swagelok® cells. The working electrodes were sulfur electrodes (70% of Sulfur, 10% of Carbon and 20% of Polyethylene oxide). The auxiliary electrodes were made from the lithium foil with thickness 78 μ m (FMC Corp., USA). One layer of micro porous membrane Celgard 3401 was used as a separator. The properties of electrolyte solutions were measured by the standard methods.

The table shows some physicochemical properties of 1m solution of lithium salts in sulfolane at 30 0 C.

Some properties of 1 m lithium salt solutions in sulfolane at 30 ^oC

Table

Salt	r(A`), Å	Kass	η, mPa·s	χ , mS·cm ⁻¹	η·χ
LiCF ₃ SO ₃	3.33	50.8	33.0	0.87	28.7
LiClO ₄	3.05	24.7	35.2	2.16	76.0
LiBF ₄	3.10	9.8	32.5	1.65	53.6
LiPF ₆	3.33	3.3	38.0	2.71	103.0
LiN(CF ₃ SO ₂) ₂	4.50	2.4	33.8	2.70	91.3

 $r(A^{\bar{}})$ – anion's radios, K_{ass} – association constant, η – dynamic viscosity, χ – conductivity.

The investigation showed that properties of investigated electrolytes influenced at the length and potential of the plateaus of discharge curves of lithium sulfur cells (fig. 1) and on the character of change of discharge capacity of cells during long-time chargedischarge cycling.

Analysis of obtained data shows that the initial discharge capacity of lithium sulfur cells increases with the rising of association constant of lithium salts in sulfolane except solutions of LiBF₄ in sulfolane (fig. 2). The character of changes of capacity of lithium sulfur cells during cycling depends on the properties of electrolyte (fig. 3). The initial rate of capacity depletion reduces in the following sequence: LiN(CF₃SO₂)₂ > LiClO₄ > LiAsF₆ ≈ LiPF₆ > LiCF₃SO₃ > LiBF₄.

From obtained results it is possible to conclude that the increasing of association constant of lithium salts reduces to:

- reducing of conductivity of electrolyte solutions;
- reducing of potential of plateaus of the discharge curves;
- increasing of specific discharge capacity;
- reducing of the initial rate of degradation of capacity of lithium-sulfur cells.



Fig. 1. The first discharge curves of Lithium-Sulfur cells. $I_{discharge}$ =0,2 mA/cm²; I_{charge} =0,1 mA/cm², ΔU =1,5÷2,8 V, t= +30 ^{0}C .



Fig. 2. Dependences of cell properties on the association constant of lithium salts in sulfolane. **1** – mean voltage of 1^{st} plateau; **2** – mean voltage of 2^{nd} plateau; **3** – discharge capacity of 1^{st} plateau; **4** – discharge capacity of 2^{nd} plateau; **5** – total discharge capacity. Unfilled markers correspond to LiBF₄.



Cycle number

Fig. 3. The capacity fade of Lithium-Sulfur cells during charge-discharge cycling.

Literature

1. Kolosnitsyn V.S., Karaseva E.V. // Russian Journal of Electrochemistry, 2008, Vol. 44, No. 5, pp. 506–509.

This work was supported by Oxis Energy Ltd. (UK) under contract no. 17141/6-07.