Relationship between composition of the electrolyte solutions and energetic performance of 1.5 V non-aqueous cells of lithium/iron sulfide system

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Abstract

Seven electrolyte solutions in equimolar solvent mixtures or in one-component solvents have been selected on the basis of own results of research and on literature data: $LiAsF_6$ in GBL + 1,2-DME; $LiClO_4$ in GBL + 1,2-DME; $LiClO_4$ in GBL + 2-MeTHF; $LiAsF_6$ in PC; $LiClO_4$ in PC; $LiAsF_6$ in AN + PC, and $LiClO_4$ in AN. They were the basis for constructing seven series of the miniaturized coin-type R43 lithium cells with the Li/FeS electrode system. Relationship between composition of the electrolyte solutions and energy performance of the cells was studied for over 4800 h (200 days). The open-circuit voltage (emf) and the discharge curves (voltage U versus time t) were determined for two load values $R = 100$ kΩ and $R = 22$ kΩ. The practical electric charge capacity Q_p, the practical energy capacity E_p, the weights of the spent electrode materials (lithium m_{Li} and iron sulfide m_{FeS}), the practical specific energy E_{ps}, the electric charge and energy efficiency coefficients, η_{Qp}, η_{Eps}, were calculated. The best practical specific energy E_{ps} has been obtained by cells with the solution of $LiAsF_6$ in equimolar mixture AN + PC.

Introduction

The choice of the electrolyte solution is an essential problem concerning non-aqueous cells with lithium as the anode material to assure a sufficiently high-electric conductance of the inner circuit of the cell and the chemical and electrochemical stability of the components of solution during the cell work. It has been known that the electromotive force of the cell at equilibrium is determined by the electrode system [1] — whereas the real electrode potentials (depending on the Gibbs solvation energy), the working voltage of the cell and the possibility to exhaust completely the electrode materials, used in the cell depend on the electrolyte solution properties [2].

It is also known now that the molecules of the solvents and salts used hitherto undergo in part electrochemical, and chemical reactions with the Li electrode in the potential field of the given electrode system [3–6]. The passivating layers, formed in this way, at the interface play an important role — they confer a kinetic stability to

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the Li electrode. The problem consists in choosing the electrolyte solution components in such a way that the reaction products with the electrode materials yield a sufficiently thin passivation layer which would not hamper the current reaction after closing the electric circuit [7].

The quality of the constructed Li cell is given by its practical energy parameters: the capacity of the electric charge Q_p, the energy capacity E_p, the specific energy E_{ps}, and the energy efficiency coefficient $\eta_{E_{ps}}$. Theoretically, these values can be calculated from the thermodynamical data: the variations in free energy, ΔG^0, and enthalpy, ΔH^0, of the electrochemical reaction occurring in the cell [1]. Thus, the practical energy parameter values of the cell depend also on the properties of the electrolyte solution, on the electrode materials preparation, and on the cell construction.

Since few years we have investigated [8–10] the 1.5 V Li cell with iron sulfide, FeS, as the cathode material. The synthesis of the porous cathode material is presented in ref. 8. The cell has the advantages: the high theoretical specific energy values, 1037 W h/kg [1], the working voltage 1.5 V, and cheap and harmless FeS material. The system was hitherto studied by McCoy et al. [11], Uetani et al. [12], Iwakura et al. [13], and by others [14–16]. However, they did not obtain the attainable practical energy efficiency.

It has been the purpose of this work to find the relationship between the practical energy efficiency values of the cells based on the Li/FeS electrode system and their electrolyte compositions selected on the basis of our studies presented in our work [17], and in literature data [18–20].

Experimental

Seven electrolyte solutions in equimolar two-component mixtures or in one-component solvents were selected on the basis of our studies of electrical conductance and physicochemical properties presented in refs. 17 and 20 and other literature sources [18, 19], Fig. 1:

1. $LiAsF_6$ in equimolar GBL + 1,2-DME mixture
2. $LiClO_4$ in equimolar GBL + 1,2-DME mixture
3. $LiClO_4$ in equimolar GBL + 2-MeTHF mixture
4. $LiAsF_6$ in PC
5. $LiClO_4$ in PC
6. $LiAsF_6$ in equimolar AN + PC mixture
7. $LiClO_4$ in AN

where GBL: γ-butyrolactone; 1,2-DME: 1,2-dimethoxyethane; 2-MeTHF: 2-methyltetrahydrofuran; PC: propylene carbonate, and AN: acetonitrile.

They were used for constructing seven series (70 pieces, 10 cells each) of the miniaturized coin-type R43 Li cells based on the Li/FeS electrode system. The number of the series is the same as the number of the solution.

The cathode material, porous semiconducting FeS, was of our own synthesis [8, 9]. The cells were assembled, Fig. 2, in collaboration with the Central Laboratory of Batteries and Cells (CLAiO) in Poznań by the methods elaborated by us and by CLAiO [21, 22].

The energy performance of the cells were studied for over 4800 h (200 days). The open-circuit voltage (emf) and the discharge curves (voltage U versus time t) were determined for the two load values: $R = 100$ kΩ and $R = 22$ kΩ, Figs. 3–8.
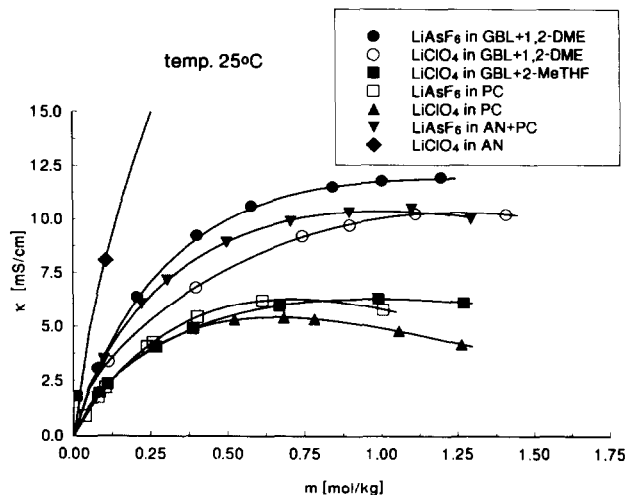
Fig. 1. Specific conductance κ, as a function of molality m, seven electrolyte solutions selected for constructing seven series of Li/FeS cells [17]: κ_{max} at 25 °C for the studied systems; (O) 11.9 mS/cm, (⊙) 10.3 mS/cm, (■) 8.7 mS/cm, (□) 6.3 mS/cm, (▲) 5.4 mS/cm, (▼) 10.4 mS/cm, (♦) 2.3 mS/cm, respectively. The solid lines fitting of the Casteel–Amis equation to the experimental points of the studied systems.
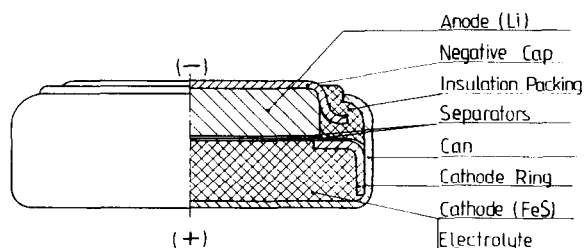

Fig. 2. Schematic illustration of the Li/FeS cell, type R43.

Results and discussion

The following parameters have been calculated from the discharge curves — voltage U versus time t and current intensity i versus time t — for two load values $R = 100$ kΩ, and $R = 22$ kΩ:

(i) the practical capacity of electric charge, Q_p in (C) and (mA h):

$$Q_p = \int_0^t i(t) \, dt \tag{1}$$

(ii) the weights of spent electrode materials, lithium, m_{Li}, and iron sulfide, m_{FeS} in g

(iii) the practical energy capacity, E_p in (J):
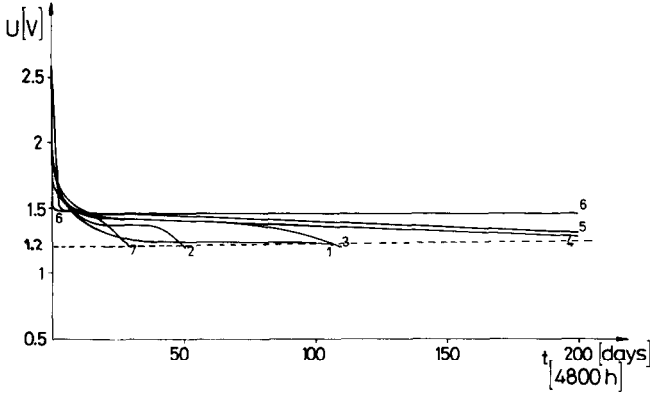
$$E_p = \int_0^t U(t) \, i(t) \, dt \tag{2}$$

Fig. 3. Discharge characteristic (voltage U vs. time t) for seven series of the Li/FeS cells, type R43, on the constant load value $R = 100$ kΩ, at temperature: 20 °C.
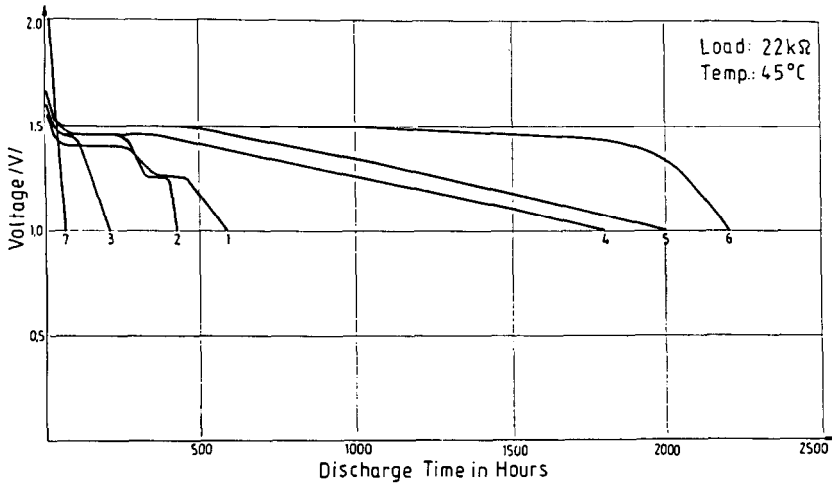

Fig. 4. Discharge characteristics (voltage U vs. time t) for seven series of the Li/FeS cells, type R43, on the constant load value $R = 22$ kΩ, at temperature: 45 °C.

(iv) the practical specific energy E_{ps} in (J/g) and (W h/kg):

$$E_{ps} = \int_0^t U(t)\, i(t)\, dt / m_{Li} + m_{FeS} \tag{3}$$

(v) the practical capacity of electric charge and the practical specific energy efficiency coefficients, η_{Qp}, η_{Eps}, as:

$$\eta_{Qp} = Q_p / Q_T \quad \text{and} \quad \eta_{Eps} = E_{ps} / E_{Ts} \tag{4}$$

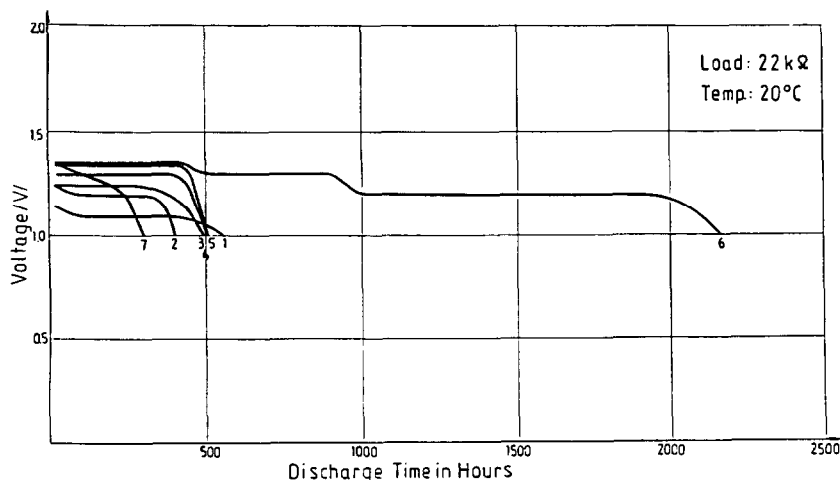where Q_T is the theoretical electric charge capacity and E_{Ts} the theoretical specific energy.

Fig. 5. Discharge characteristics (voltage U vs. time t) for seven series of the Li/FeS cells, type R43, on the constant load value $R = 22$ kΩ, at temperature: 20 °C.
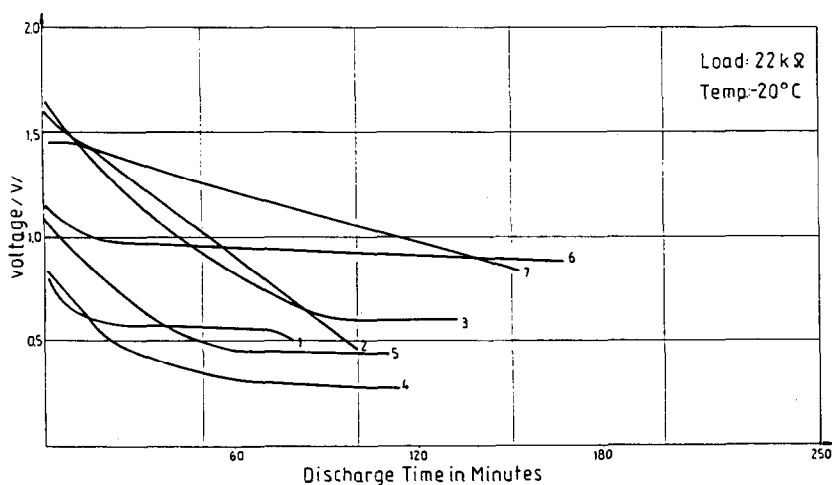

Fig. 6. Discharge characteristics (voltage U vs. time t) for seven series of the Li/FeS cells, type R43, on the constant load value $R = 22$ kΩ, at temperature: −20 °C.

Results of calculations are presented in Table 1 for $R = 100$ kΩ and in Table 2 for $R = 22$ kΩ, together with the emf data. As we see, the highest practical capacity of electric charge efficiency coefficient, $\eta_{Qp} = 0.99$ and the practical specific energy efficiency coefficient, $\eta_{Eps} = 0.60$ have been obtained for the cells filled with the solution of LiAsF$_6$ in equimolar mixture of AN + PC (series No. 6), Table 2.

The cells series No. 6, when discharged at $R = 100$ kΩ at 20 °C, yielded the voltage value of 1.5 V (Fig. 3) and the current value of about 14 μA, during the very long time, above 4800 h.

On $R = 22$ kΩ load, the series No. 6 cells keep the $U = 1.5$ V voltage also at 45 °C for about 1500 h (Figs. 4–7).

TABLE 1

Li/FeS cells, coin-type R43. Relationship between composition of the electrolyte solutions and energy parameters of the cells

No. of solutions (series)	emf (V)	Q_p (C)	Q_p (mA h)	η_{Qp}	m_{Li} (g)	m_{FeS} (g)	E_p (J)	E_{ps} (J/g)	E_{ps} (W h/kg)	η_{Eps}	Discharge up to 1.2 V (days)
1	2.23	184.3	51.2	0.29	0.0133	0.0840	214.9	551.2	153.1	0.17	110
2	2.16	89.9	24.9	0.14	0.0065	0.0410	101.7	308.2	85.6	0.09	50
3	2.55	165.8	46.0	0.26	0.0120	0.0756	212.0	642.4	178.4	0.20	110
4	2.50	217.2	60.3	0.35	0.0156	0.0990	293.8	890.3	247.3	0.28	>200
5	2.67	235.4	65.4	0.38	0.0170	0.1070	336.3	1019.1	283.1	0.31	>200
6	1.56	235.0	65.3	0.38	0.0170	0.1070	342.5	1037.9	288.3	0.32	▲200
7	2.20	62.0	17.2	0.10	0.0045	0.0282	79.1	239.7	66.6	0.07	39

[a]Emf of the cells, practical electric charge capacity Q_p; weight of the spent electrode materials m_{Li} and m_{FeS}; practical energy capacity E_p; practical specific energy E_{ps}, and the practical efficiency coefficients η_{Qp}, η_{Eps}; value of load R: 100 kΩ, temperature: 20 °C, time of discharge: 200 days (4800 h).

TABLE 2

Li/FeS cells, coin-type R43. Relationship between composition of the electrolyte solutions and energy parameters of the cells

No. of solutions (series)	emf (V)	Q_p (C)	Q_p (mA h)	η_{Qp}	m_{Li} (g)	m_{FeS} (g)	E_p (J)	E_{ps} (J/g)	E_{ps} (W h/kg)	η_{Eps}
1	2.27	209.6	58.2	0.33	0.0151	0.0955	182.5	553.0	153.6	0.17
2	2.08	116.5	32.4	0.19	0.0084	0.0531	106.4	322.4	89.5	0.10
3	2.60	160.4	44.5	0.26	0.0115	0.0729	168.0	509.1	141.4	0.16
4	2.74	472.3	131.2	0.75	0.0340	0.2150	334.7	1014.2	281.7	0.31
5	2.64	505.4	140.4	0.80	0.0363	0.2300	381.4	1155.7	321.0	0.36
6	1.57	624.0	173.3	0.99	0.0449	0.2820	637.4	1931.5	536.5	0.60
7	2.40	75.4	20.8	0.12	0.0054	0.0343	78.8	238.8	66.3	0.07

[a]Emf of the cells; practical electric charge capacity Q_p; weight of the spent electrode materials m_{Li} and m_{FeS}; practical energy capacity E_p; practical specific energy E_{ps}, and the practical efficiency coefficients η_{Qp}, η_{Eps}, value of load R: 22 kΩ, temperature 20 °C.
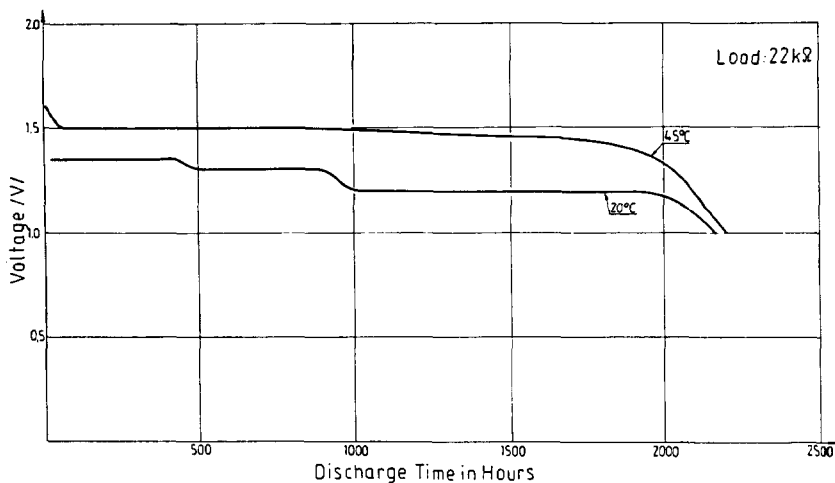
Fig. 7. Discharge characteristics (voltage U vs. time t) for the series No. 6 of the Li/FeS cell, type R43, on the constant load value $R = 22$ kΩ, at temperature: 45 and 20 °C.
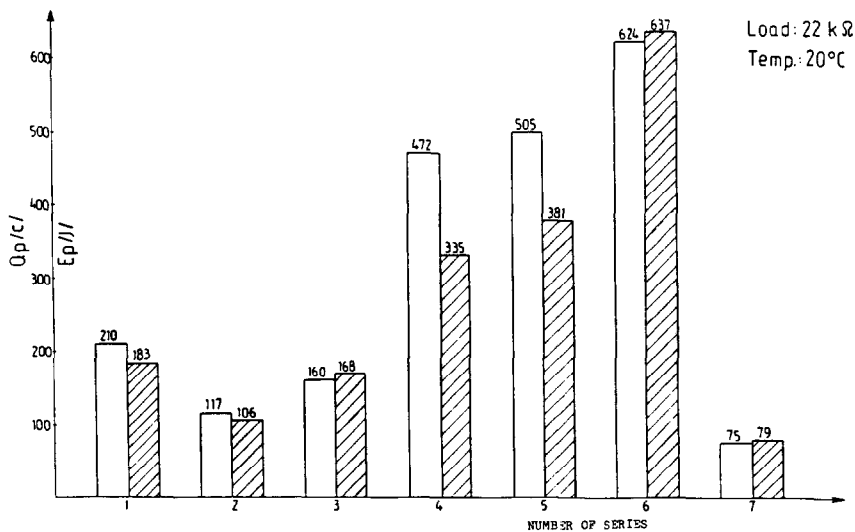

Fig. 8. The practical charge capacity Q_p, and the practical energy capacity E_p, with respect to the seven compositions of the electrolyte solutions on the constant load value $R = 22$ kΩ, at temperature: 20 °C.

Figures 5 and 6 present the changes of the voltage versus time at 20 °C and −20 °C for the cells loaded with $R = 22$ kΩ.

On full discharge at $R = 22$ kΩ, the cells of series No. 6 gave almost 100% value of the theoretical electric charge capacity, ($Q_T = 625.6$ C or 174 mA h; $Q_p = 624.0$ C or 173 mA h) and practical specific energy $E_{ps} = 536.5$ W h/kg.

Being discharged with low current ($R = 100$ kΩ), the cells of No. 4 and No. 5 series filled with LiClO$_4$ and LiAsF$_6$ in PC solutions behave similarly to the series No. 6 cells (Fig. 3).

At thermodynamic equilibrium the values of the theoretical energies parameters for electrodic Li/FeS system are as follows: the theoretical energy capacity (for 1.7 V average emf value) $E_T = 1063.5$ J. The cell type R43 contains 0.045 g of Li and stoichiometric value of FeS = 0.285 g; hence the theoretical specific energy of the cell is $E_{Ts} = 3222.3$ J/g, or 895 W h/kg. The E_{Ts} value as calculated from standard thermodynamic functions [1] is higher and equals to 3733.0 J/g or 1037 W h/kg.

Conclusions

The best energy performance of the Li/FeS electrode system has been obtained by the cells with the solution of $LiAsF_6$ in equimolar mixture of AN + PC.

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