Comparative study of LiBF$_4$, LiAsF$_6$, LiPF$_6$, and LiClO$_4$ as electrolytes in propylene carbonate–diethyl carbonate solutions for Li/LiMn$_2$O$_4$ cells

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Abstract

The specific conductances of LiClO$_4$, LiPF$_6$ and LiAsF$_6$ in concentrated solutions of propylene carbonate (PC)–diethyl carbonate (DEC) mixtures at 15, 20, 25, 30, 35 and 40 °C were measured and the data were treated with an empirical equation. Specific conductances, against concentration, temperature, and solvent composition plots are given, as well as concentration that corresponds to the maximum specific conductance, against concentration. Activation energies were also calculated from temperature dependence of specific conductance. The three salts mentioned above, as well as LiBF$_4$, were tested as electrolyte solutions with PC–DEC, in Li/Li$_{1.05}$Mn$_2$O$_4$ cells.
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1. Introduction

There is no doubt that one of the most exciting areas in electrochemistry nowadays relates to the development of "rocking-chair" type Li-ion batteries and generally to high-energy batteries [1]. Spinel manganese oxides Li$_x$Mn$_2$O$_4$, are among the promising cathode materials for lithium secondary batteries and some attractive properties have been reported [2,3]. When Li$^+$ ions are intercalated/deintercalated in the range of $x = 0$–1 the output potential of the Li/Li$_x$Mn$_2$O$_4$ cell is about 4 V, whereas when in the range of $x = 1$–2 the cell discharges at about 3 V [4].

Various organic solvents have been tested for lithium secondary cells as electrolyte solutions but the results are still not very satisfactory [5]. As is well known, the conductivity of the electrolyte solution is an important factor in the performance of the battery. The conductivity of the electrolyte solution can be improved by mixing solvents of high dielectric constant, well disposed for electrolyte dissociation, with solvents of low viscosity, which are favorable for ion mobility [6].

One high dielectric constant ionogenic solvent, widely studied for Li cells is propylene carbonate (PC) [7,8], as well as mixtures of it with low viscosity liquids [6]. It is true

that PC based electrolytes are not suitable for Li-ion batteries due to problems of passivation of graphite electrodes. However when a cosolvent is introduced in the solution, the reversibility of Li/graphite cells can be improved [9]. Diethyl carbonate (DEC) is a cosolvent often used because of its low viscosity [10]. Although PC–DEC system is not expected to be suitable for Li-ion batteries, there is no lack of interest in the study of it. Conductances of various salts in mixtures of PC with other solvents have been measured in our laboratory [11–13], whereas viscosity and relative permittivity behavior of PC–DEC mixtures as well as conductometric behavior of LiBF$_4$ in PC–DEC mixtures has been reported in a previous paper [14].

In this paper our study in PC–DEC system is being completed by presenting the conductometric behavior of three of the most popular salts [15] for lithium battery investigations: LiAsF$_6$, LiPF$_6$, and LiClO$_4$ in highly concentrated solutions with PC–DEC mixtures. The performance of Li/Li$_{1.05}$Mn$_2$O$_4$ cell with the electrolyte solutions of LiBF$_4$, LiAsF$_6$, LiPF$_6$, and LiClO$_4$ in PC–DEC is also discussed.

2. Experimental

PC (Aldrich, 99%) and DEC (Merck, >99.9%) were treated by distillation and molecular sieves 4 Å. LiClO$_4$ (Vetron, GmbH, min 99.5%) was recrystallized from conductivity water and dried at 170 °C. LiAsF$_6$ (Lithco,

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electrochemical grade) was vacuum dried. LiPF$_6$ (Aldrich, +99.99%) was used as received.

All solutions were prepared by mass with a Shimadzu AEG-220 analytical balance of four decimal places. Solutions were prepared in a glove box, where humidity was not more than 2 ppm.

Glass cells with platinized electrodes, in order to minimize polarization effects [16,17], were used for conductance measurements. Cells constants (11.91, 25.28 and 44.9 cm^{-1}) were determined with aqueous potassium chloride solutions. Details about aqueous potassium chloride solutions preparations are given elsewhere [13]. A Beckman (RC—18 A) conductivity bridge was used for conductance measurements, whereas the temperature was controlled by a Leeds and Northrup 4956 thermostat. Measurements were taken at 1 and 3 kHz; no differences were found at the two frequencies and extrapolation to infinitive frequency was not necessary.

Lithiated spinel manganese dioxide was prepared by solid-state reaction of commercially available electro-chemical MnO$_2$ (Tosoh Hellas) with Li$_2$CO$_3$ (Aldrich). The Li content of the final product was determined by atomic absorption spectroscopy. Details about Li$_{1.05}$Mn$_2$O$_4$ preparation and structural information are given elsewhere [18].

Two electrode cells, with electrodes of 12 mm diameter, were used. Cathode electrode was formed by pressing a mixture of the active material with Teflonized Acetylene Black in a 80:20 ratio onto aluminum disk current collector. The electrode masses varied between 9 and 13 mg. Pure Li foil, 0.38 mm thick (Aldrich 99.9%) was used as anode material. The electrodes were separated by a Whatman GF/C separator, soaked in the electrolyte solution, which was 1 m of the studying salt in PC 50.7%–DEC 49.3%.

Electrochemical measurements were conducted galvanostatically using two electrode cells and an Arbin battery test system. Galvanostatic measurements were performed with a charge/discharge rate of $C/8$.

3. Results and discussion

The specific conductances and the corresponding concentrations are given in Table 1 for LiClO$_4$, in Table 2 for LiPF$_6$ and in Table 3 for LiAsF$_6$. Comparing the experimental results of LiClO$_4$ and LiPF$_6$ for PC 50.7%–DEC 49.3% at 20, 30 and 40 °C with the corresponding curves given by Hayashi et al. [19] a good agreement can be seen.

Conductance data analysis of concentrated solutions usually are achieved by means of empirical functions [20]. Such an equation is the following, which can be attached to systems with maximum in κ–m curves and has the advantage to give the value zero for the specific conductance when molality becomes zero

$$\kappa = m^a \exp(bm^2 + cm + d). \qquad (1)$$

Table 1

Specific conductances $\kappa \times 10^4$ (S cm^{-1}) and the corresponding concentrations m (mol kg^{-1}) of LiClO$_4$ in PC + DEC mixtures

m	κ					
	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
PC 10.7%–DEC 89.3%						
0.195	2.454	2.599	2.741	2.877	3.013	3.152
0.321	4.788	5.102	5.413	5.720	6.011	6.307
0.502	7.745	8.301	8.869	9.421	9.935	10.459
0.858	12.853	13.914	14.961	15.964	16.994	18.023
1.101	15.013	16.359	17.713	19.004	20.316	21.638
1.241	15.862	17.351	18.857	20.298	21.755	23.229
1.395	16.661	18.301	19.933	21.520	23.144	24.790
1.598	17.044	18.831	20.577	22.328	24.117	25.945
1.702	16.944	18.780	20.556	22.378	24.224	26.123
PC 29.2%–DEC 70.8%						
0.180	13.056	14.027	14.94	15.846	16.725	17.603
0.394	19.599	21.162	22.672	24.181	25.680	27.136
0.517	22.256	24.141	25.963	27.772	29.562	31.338
0.827	25.808	28.208	30.562	32.888	35.272	37.633
1.096	26.280	28.950	31.659	34.308	37.008	39.800
1.186	26.040	28.742	31.538	34.266	37.039	39.945
1.312	25.420	28.068	30.927	33.719	36.581	39.582
1.667	22.906	25.017	27.912	30.781	33.759	36.856
1.758	22.235	24.092	26.955	29.815	32.799	35.865
PC 50.7%–DEC 49.3%						
0.205	25.896	28.171	30.394	32.594	34.781	37.023
0.389	34.406	37.512	40.673	43.775	46.851	50.102
0.536	37.877	41.561	45.159	48.745	52.329	56.066
0.788	38.831	43.270	47.227	51.303	55.527	59.716
0.926	37.951	42.433	46.474	50.691	54.972	59.304
1.111	35.422	39.862	43.964	48.275	52.649	57.124
1.308	32.039	36.206	40.349	44.664	49.029	53.613
1.594	26.848	30.501	34.631	38.780	42.996	47.550
1.726	24.475	28.009	32.054	36.031	40.147	44.518
PC 70.4%–DEC 29.6%						
0.240	32.318	35.507	38.735	41.930	45.223	48.499
0.378	39.570	43.456	47.615	51.590	55.833	59.997
0.521	43.521	48.003	52.785	57.380	62.271	67.117
0.791	44.031	49.208	54.501	59.781	65.238	70.837
0.949	41.675	46.983	52.312	57.730	63.259	69.041
1.194	36.206	41.359	46.538	51.871	57.310	63.106
1.360	32.104	36.971	41.967	47.094	52.399	58.063
1.609	26.203	30.550	35.186	39.911	44.955	50.268
1.790	22.241	26.316	30.599	35.062	39.858	44.825
PC 90.2%–DEC 9.8%						
0.194	27.163	30.142	33.135	36.126	39.213	42.339
0.545	44.131	49.511	54.889	60.520	66.141	71.815
0.611	44.659	50.244	55.854	61.683	67.527	73.467
0.898	41.663	47.558	53.573	59.661	65.946	72.472
1.094	37.040	42.779	48.645	54.598	60.875	67.412
1.381	29.589	34.818	40.143	45.742	51.745	57.959
1.266	32.555	38.018	43.585	49.338	55.487	61.863
1.690	21.772	26.238	30.973	36.026	41.294	46.945
1.734	20.589	24.926	29.606	34.552	39.652	45.220

In the above equation κ is the specific conductance, m the molality and a, b, c and d constants. If μ is the molality that corresponds to the maximum conductivity, $\kappa_{(max)}$, constants a and b in Eq. (1) can be determined in the following way. Taking the first derivative with respect to m and setting it

Table 2
Specific conductances $\kappa \times 10^4$ (S cm^{-1}) and the corresponding concentrations m (mol kg^{-1}) of LiPF$_6$ in PC + DEC mixtures

m	κ					
	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
PC 10.7%–DEC 89.3%						
0.212	8.685	9.282	9.826	10.378	10.877	11.368
0.396	17.796	19.047	19.894	21.086	22.228	23.362
0.57	24.847	26.714	28.541	30.332	32.091	33.871
0.701	29.530	31.879	34.191	36.417	38.615	40.874
0.946	36.092	39.264	42.265	45.238	48.153	51.230
1.178	39.267	43.025	46.624	50.191	53.631	57.336
1.307	39.939	43.934	47.693	51.530	55.202	59.183
1.599	39.124	43.408	47.144	51.400	55.501	59.930
1.742	37.241	41.480	45.839	50.194	54.503	59.080
PC 29.2%–DEC 70.8%						
0.197	20.331	21.996	23.621	25.206	26.807	28.370
0.386	35.623	38.775	41.726	44.723	47.662	50.693
0.57	44.721	48.812	52.759	56.723	60.655	64.632
0.791	50.126	54.954	59.769	64.508	69.330	74.075
0.994	51.452	56.719	62.066	67.296	72.693	77.977
1.188	50.673	56.285	61.931	67.470	73.230	78.952
1.377	48.837	54.654	60.424	66.186	72.142	78.198
1.601	45.959	51.949	57.664	63.487	69.420	75.667
1.83	42.762	48.475	53.905	59.603	65.232	71.129
PC 50.7%–DEC 49.3%						
0.188	28.844	31.454	33.993	36.559	39.093	41.789
0.388	37.798	41.999	45.219	48.908	52.911	56.904
0.512	43.650	48.058	52.402	56.789	61.142	65.642
0.859	58.206	64.809	71.742	78.579	85.576	92.565
1.054	57.495	63.850	70.912	77.814	84.993	92.432
1.231	53.297	60.393	67.674	74.984	82.396	90.136
1.412	48.100	55.014	62.004	69.013	76.298	84.651
1.588	41.930	48.317	55.448	62.304	69.727	77.178
1.702	38.305	43.991	50.814	57.524	65.112	72.088
PC 70.4%–DEC 29.6%						
0.177	19.113	20.919	22.681	24.447	26.33	28.196
0.358	43.423	46.831	51.043	55.012	59.045	63.985
0.512	53.654	59.903	66.251	72.729	79.05	85.747
0.599	56.296	63.001	70.033	76.291	82.999	90.498
0.904	55.603	63.056	70.909	78.655	86.873	95.048
1.271	47.845	55.513	63.22	71.352	79.713	88.532
1.493	42.026	49.586	56.863	64.952	72.802	81.123
1.685	36.014	42.743	49.847	57.112	64.927	73.277
1.754	33.423	39.963	46.968	53.904	61.68	70.253
PC 90.2%–DEC 9.8%						
0.200	27.750	30.911	34.066	37.239	40.417	43.722
0.399	44.235	48.562	53.674	59.214	66.057	74.003
0.536	49.444	55.926	62.463	69.123	75.956	83.182
0.742	50.993	58.252	65.922	72.536	79.999	87.987
0.910	48.675	56.280	64.130	72.180	80.463	89.278
1.101	44.636	51.912	59.042	67.821	76.244	85.753
1.307	37.640	44.823	52.429	60.498	68.789	77.722
1.523	30.001	36.931	43.563	51.467	59.568	67.524
1.730	23.201	28.910	35.135	41.796	49.079	56.999

Table 3
Specific conductances $\kappa \times 10^4$ (S cm^{-1}) and the corresponding concentrations m (mol kg^{-1}) of LiAsF$_6$ in PC + DEC mixtures

m	κ					
	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
PC 10.7%–DEC 89.3%						
0.207	10.441	11.242	12.001	12.713	13.431	14.103
0.375	22.213	23.358	24.965	25.908	26.936	27.953
0.602	32.213	34.922	37.605	40.230	42.797	45.383
0.658	34.630	37.018	39.996	42.687	45.365	48.075
0.982	42.466	46.504	50.416	54.314	58.121	62.079
1.102	44.522	48.895	53.011	57.118	61.087	65.611
1.451	48.027	53.367	58.745	64.123	69.587	75.137
1.589	48.546	54.168	59.761	65.354	70.804	76.642
PC 29.2%–DEC 70.8%						
0.207	26.799	29.017	31.242	33.406	35.708	37.914
0.384	39.141	42.807	46.553	50.423	54.308	58.213
0.57	50.216	54.514	59.302	64.923	68.699	73.528
0.644	52.564	56.907	61.941	67.639	72.356	78.423
0.966	57.815	63.930	70.375	76.851	82.978	89.483
1.089	56.992	63.014	69.942	76.386	82.882	89.612
1.410	52.929	59.73	66.644	73.612	80.848	88.23
1.571	49.064	56.053	63.812	70.225	77.256	85.639
PC 50.7%–DEC 49.3%						
0.428	55.014	61.004	66.786	71.863	77.862	83.725
0.512	56.668	62.706	68.789	74.494	80.975	87.321
0.641	58.968	65.842	72.057	78.553	85.616	93.085
0.868	61.27	68.837	76.38	84.009	91.881	100.05
1.104	57.842	65.824	73.772	82.043	90.763	99.086
1.163	56.306	64.217	72.375	80.553	88.932	97.737
1.528	45.162	53.024	60.386	68.235	76.901	85.601
1.607	42.499	49.956	57.574	65.550	73.750	82.525
PC 70.4%–DEC 29.6%						
0.187	31.342	34.69	37.962	41.281	44.649	48.147
0.305	41.001	45.121	49.625	54.028	58.852	63.215
0.489	51.022	56.974	63.079	69.200	75.47	81.987
0.568	51.985	58.111	65.099	72.055	79.565	86.686
0.856	53.915	61.218	68.966	76.589	84.691	92.957
1.130	50.001	58.005	66.123	74.215	82.916	91.993
1.226	48.202	56.147	64.268	72.743	81.622	91.027
1.369	44.825	52.575	60.614	69.182	78.886	87.986
PC 90.2%–DEC 9.8%						
0.250	35.884	40.161	44.438	48.788	53.204	57.862
0.318	40.653	45.865	50.011	55.860	60.986	66.224
0.495	49.059	55.422	61.180	68.558	75.237	82.442
0.561	50.825	58.011	64.253	72.005	79.403	87.112
0.728	52.374	60.036	67.783	75.757	84.050	92.830
1.025	46.828	54.952	63.042	71.525	80.925	89.982
1.115	44.304	52.121	60.331	68.877	77.864	87.461
1.385	35.002	42.563	50.568	59.760	69.002	78.820

equal to zero, one can calculate constant c in terms of a, b and μ. Eq. (1) can also be solved for constant d in terms of a, b, $\kappa_{(\max)}$, and μ. By putting the obtained expressions for c and d in Eq. (1) and by taking the logarithm, Eq. (1) results in

$$\ln\frac{\kappa}{\kappa_{(\max)}} = a\ln\left(\frac{m}{\mu}\right) + b(m-\mu)^2 - \frac{a}{\mu}(m-\mu), \qquad (2)$$

which has the general form

$$Y = a\ln\left(\frac{X}{\mu}+1\right) + bX^2 - \frac{a}{\mu}X, \qquad (3)$$

where $Y = \ln(\kappa/\kappa_{(\max)})$ and $X = m - \mu$. Constants a and b can be determined by least squares method in a way that

Table 4
Standard deviation ($\times 10^4$) and mean percentage deviation (σ) of Eq. (3) for LiClO$_4$, LiPF$_6$ and LiAsF$_6$ in PC + DEC

			15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
LiClO$_4$								
	PC 10.7%	S.D.	0.013	0.014	0.015	0.017	0.019	0.023
		σ	1.039	1.077	1.190	1.374	1.546	1.856
	PC 29.2%	S.D.	0.011	0.005	0.007	0.008	0.008	0.008
		σ	0.642	0.307	0.459	0.514	0.526	0.654
	PC 50.7%	S.D.	0.004	0.006	0.005	0.004	0.006	0.003
		σ	0.250	0.388	0.358	0.280	0.390	0.240
	PC 70.4%	S.D.	0.008	0.007	0.006	0.005	0.007	0.005
		σ	0.531	0.458	0.449	0.383	0.457	0.391
	PC 90.2%	S.D.	0.005	0.003	0.003	0.003	0.002	0.002
		σ	0.406	0.151	0.251	0.248	0.175	0.147
LiPF$_6$								
	PC 10.7%	S.D.	0.010	0.008	0.002	0.003	0.003	0.002
		σ	0.527	0.469	0.124	0179	0.110	0.132
	PC 29.2%	S.D.	0.001	0.002	0.004	0.004	0.004	0.008
		σ	0.068	0.143	0.275	0.289	0.254	0.430
	PC 50.7%	S.D.	0.057	0.064	0.074	0.081	0.083	0.088
		σ	3.709	4.029	4.721	5.275	5.391	5.967
	PC 70.4%	S.D.	0.026	0.027	0.023	0.026	0.029	0.027
		σ	1.504	1.473	1.304	1.870	1.944	1.917
	PC 90.2%	S.D.	0.010	0.019	0.016	0.011	0.027	0.034
		σ	0.624	1.309	1.045	0.728	1.808	2.258
LiAsF$_6$								
	PC 29.2%	S.D.	0.013	0.030	0.014	0.013	0.005	0.009
		σ	0.947	2.523	1.183	1.084	0.454	0.739
	PC 50.7%	S.D.	0.011	0.010	0.010	0.009	0.007	0.007
		σ	0.881	0.821	0.915	0.854	0.655	0.621
	PC 70.4%	S.D.	0.007	0.008	0.007	0.009	0.011	0.013
		σ	0.494	0.570	0.538	0.656	0.784	0.942
	PC 90.2%	S.D.	0.006	0.006	0.011	0.008	0.009	0.010
		σ	0.442	0.469	0.959	0.680	0.837	0.0962

Table 5
Calculated activation energies (kJ mol^{-1}) according to Eq. (4) for LiClO$_4$, LiPF$_6$ and LiAsF$_6$ in PC 70.4%–DEC 29.6%

	m (mol kg^{-1})	15 °C	20 °C	25 °C	30 °C	35 o	40 °C
LiClO$_4$	0.240	13.40	12.87	12.36	11.87	11.40	10.94
	0.521	14.18	13.67	13.19	12.72	12.27	11.83
	0.949	16.88	16.11	15.37	14.66	13.97	13.30
	1.360	19.90	18.96	18.06	17.18	16.33	15.50
	1.790	23.86	22.63	21.44	20.28	19.17	18.09
LiPF$_6$	0.177	12.48	12.12	11.76	11.42	11.08	10.76
	0.512	15.74	15.01	14.31	13.63	12.97	12.33
	0.904	18.11	17.24	16.40	15.59	14.80	14.04
	1.493	23.09	21.61	20.19	18.81	17.48	16.19
	1.754	25.02	23.78	22.59	21.43	20.31	19.23
LiAsF$_6$	0.187	14.14	13.58	13.03	12.50	11.99	11.50
	0.489	15.68	15.04	14.43	13.84	13.27	12.71
	0.856	18.24	17.42	16.63	15.86	15.12	14.40
	1.226	21.42	20.38	19.38	18.41	17.48	16.57
	1.369	22.54	21.57	20.63	19.72	18.84	17.99

the deviation between the experimental and the calculated values is minimum.

The standard deviation (S.D.) and the mean percentage deviation (σ) for the three salts are presented in Table 4. Comparing the deviations with those reported by Casteel and Amis [21] it can be seen that they are of the same order. Deviations also seem to be independent of the salt, showing the highest and the lowest values for LiPF$_6$.

By putting the data in the following polynominal expression

$$\ln \kappa = c_0 + c_1 T^{-1} + c_2 T^{-2},$$

where T is the temperature in Kelvin, activation energies, E, can be calculated from

$$E = -R \left(\frac{\partial \ln \kappa}{\partial (1/T)} \right). \qquad (4)$$

In the above equation R is the gas constant. An example of the calculated values for the three salts is given in Table 5. Generally activation energy is decreasing by increasing the temperature or by reducing the concentration of the salt. In dilute solutions with PC as solvent, E values are strongly temperature dependent and this is in agreement with the dependence on temperature of viscosity of cyclic esters [22].

An example of the κ–m plots are presented in Figs. 1–3 for LiClO$_4$, LiPF$_6$ and LiAsF$_6$ correspondingly. The experimental points are given with the calculated, according to Eq. (3), curves. For LiAsF$_6$ in PC 10.7%–DEC 89.3% no maxima were observed. In most cases the curves are in a very good agreement with the experimental points. Decrease in the composition of PC, or decrease in temperature, shifts the maxima to the left. Such behavior has been reported by others too [21]. Generally, for an electrolyte solution the maximum specific conductance is obtained when the conductance determining effects have established a critical energy barrier that depends almost exclusively on solvent and temperature [20].

A comparative presentation of κ–m plots for the four salts for PC 50.7%–DEC 49.3% at 25 °C, is given in Fig. 4 (the data for LiBF$_4$ were taken from [14]). The conductances follow the order LiAsF$_6 >$ LiPF$_6 >$ LiClO$_4 >$ LiBF$_4$. The maximum lies around $m \approx 1$ mol kg^{-1} for LiPF$_6$, $m = 0.9$ for LiAsF$_6$ and LiBF$_4$ and $m = 0.8$ for LiClO$_4$. Similar conclusions can be drawn for the other temperatures and solution compositions.

The maxima values of the specific conductances against temperature (for PC 50.7%–DEC 49.3%) is shown in Fig. 5. The trend is linear for all the cases. So, dependence of $\kappa_{(max)}$ on temperature, t (°C), can be expressed as

$$\kappa_{(max)} = a_1 t + a_0,$$

and $\kappa_{(max)}$ values can be calculated for temperatures where there are no measurements. On increasing the temperature
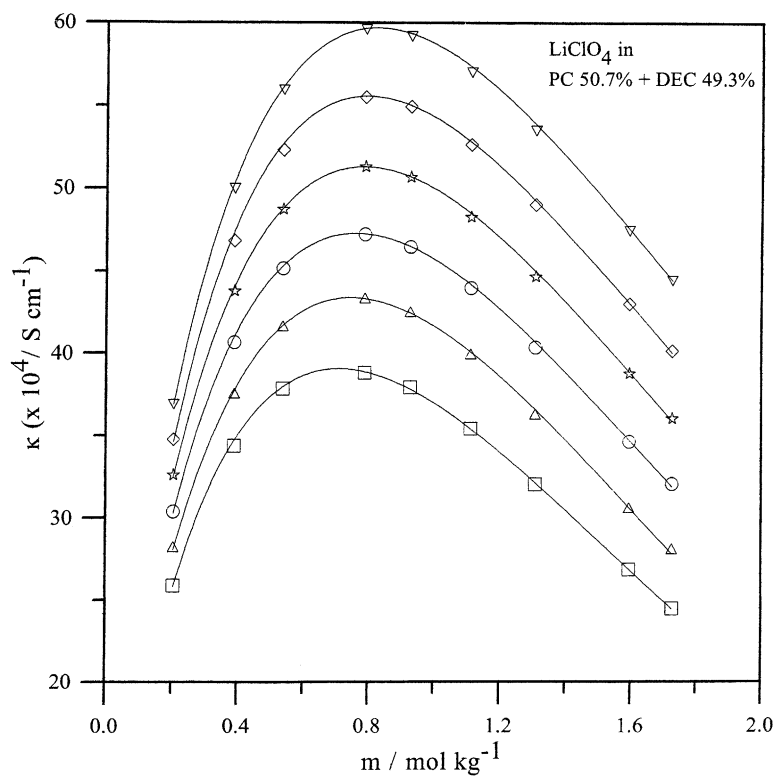
Fig. 1. Dependence of specific conductance, κ, on molality, m. The points correspond to the experimental data (squares: 15 °C; triangles: 20 °C; circles: 25 °C; stars: 30 °C; rhombs: 35 °C; reversed triangles: 40 °C) and the curves to the calculated according to Eq. (3) values.
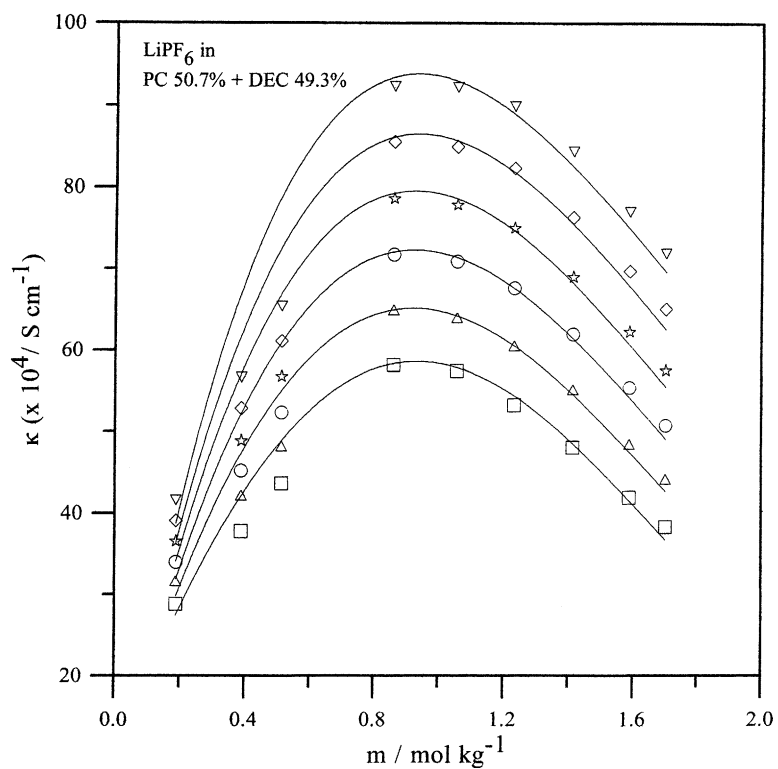

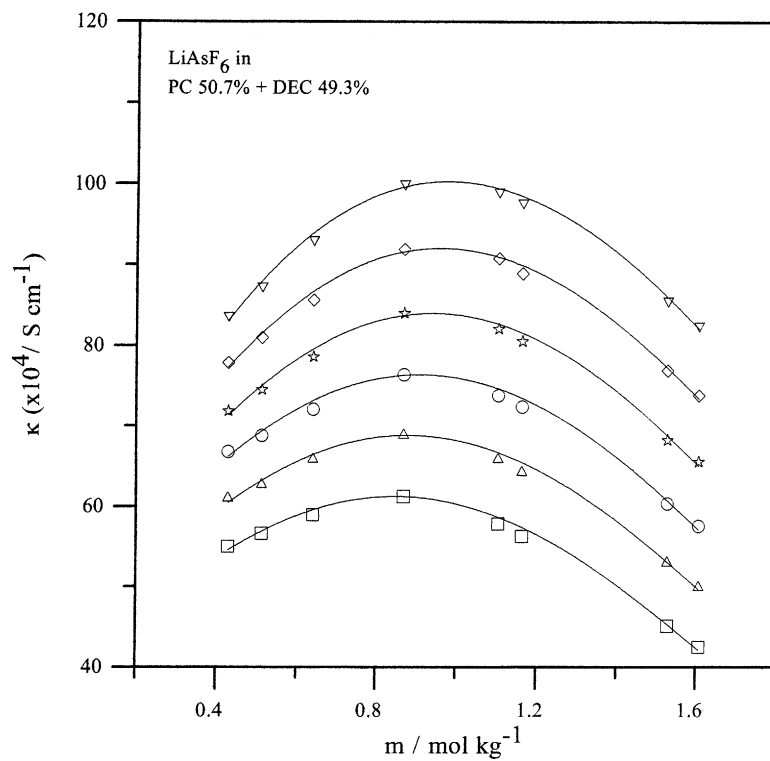Fig. 2. Symbols have the same meaning as in Fig. 1.

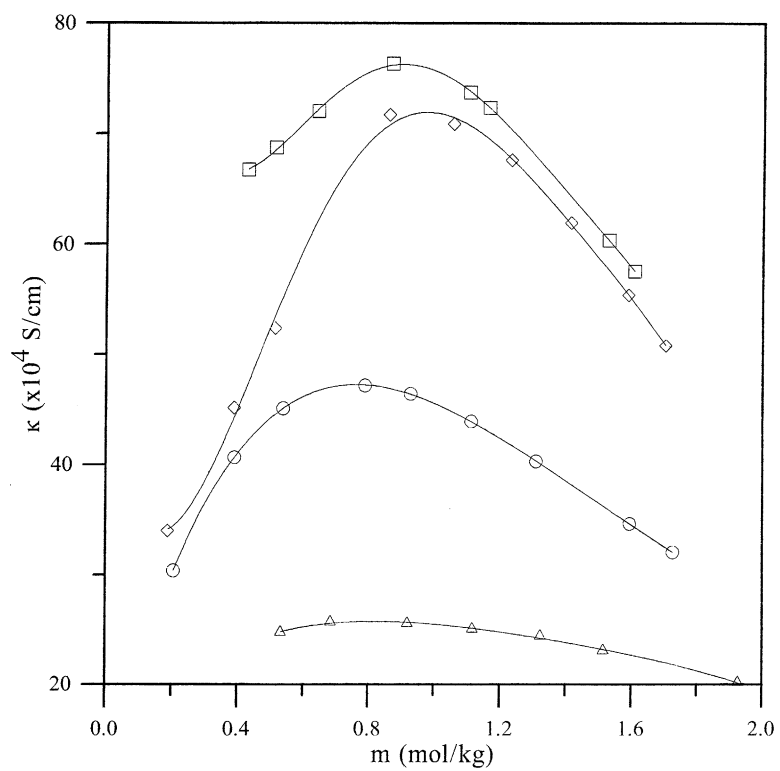Fig. 3. Symbols have the same meaning as in Fig. 1.

Fig. 4. Dependence of specific conductance, κ, on molality, m, for PC 50.7%–DEC 49.3% at 25 °C. Squares: LiAsF$_6$; rhombs: LiPF$_6$; circles: LiClO$_4$; triangles: LiBF$_4$.
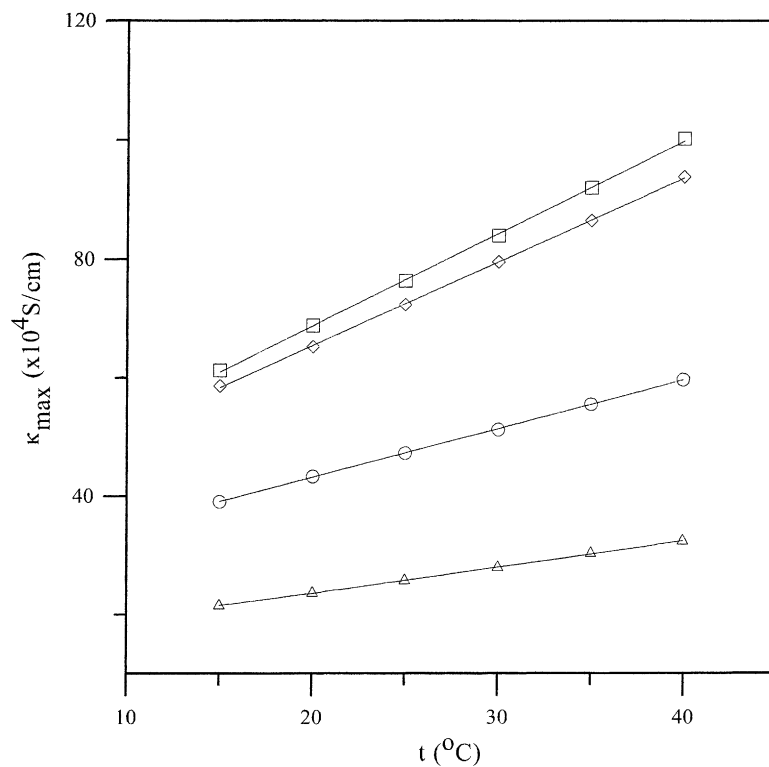
Fig. 5. Dependence of maximum specific conductance, $\kappa_{(max)}$, on temperature, t, for PC 50.7%–DEC 49.3%. Symbols have the same meaning as in Fig. 4.
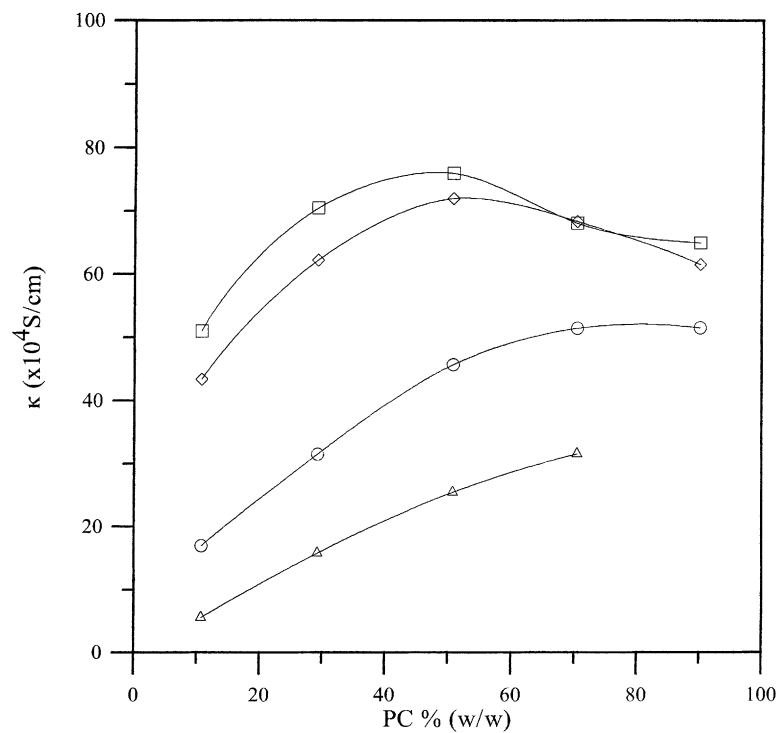
Fig. 6. Dependence of specific conductance on solvent composition for $m = 1\,mol\,kg^{-1}$, at 25 °C. Symbols have the same meaning as in Fig. 4.
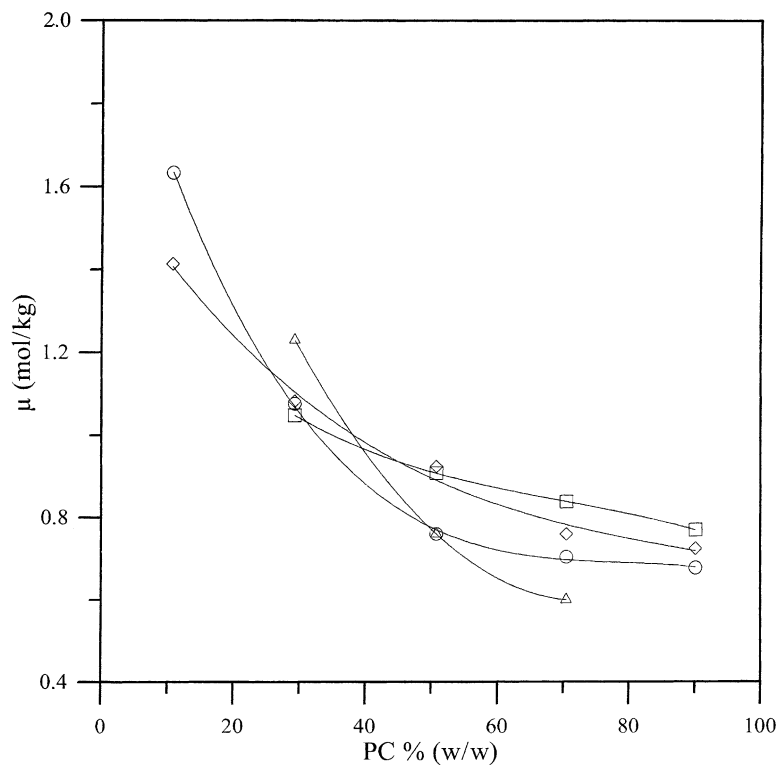
Fig. 7. Dependence of molality that corresponds to the maximum specific conductance, μ, on solvent composition, at 25 °C. Symbols have the same meaning as in Fig. 4.
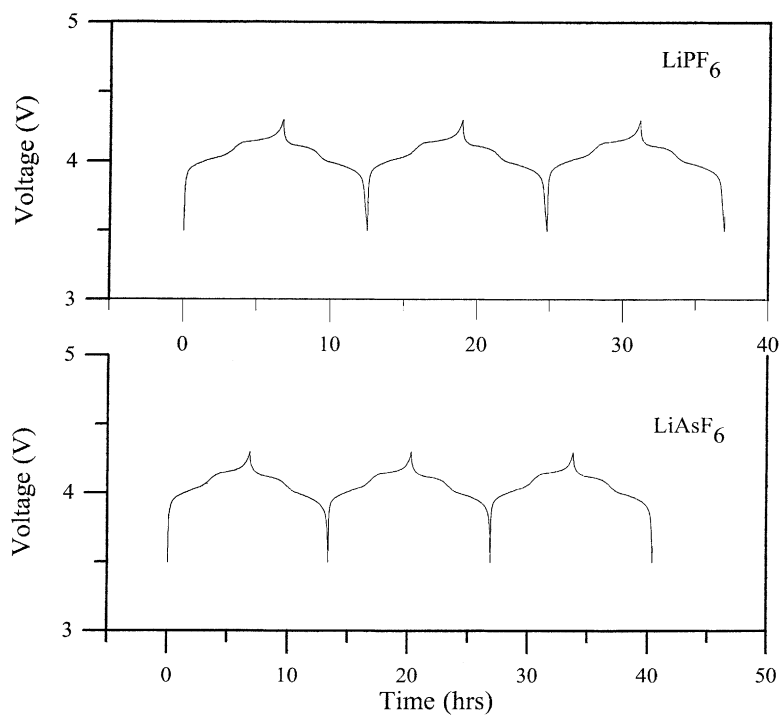
Fig. 8. Voltage–time profiles of Li/Li$_{1.05}$Mn$_2$O$_4$ cells with electrolyte solution 1 m LiAsF$_6$ and LiPF$_6$ in PC 50.7%–DEC 49.3% (temperature 25 °C).
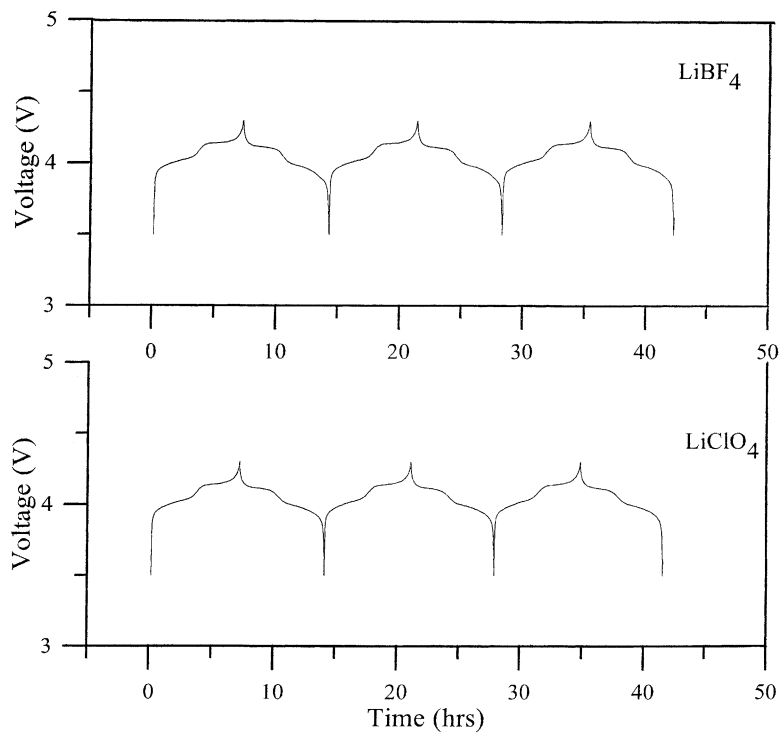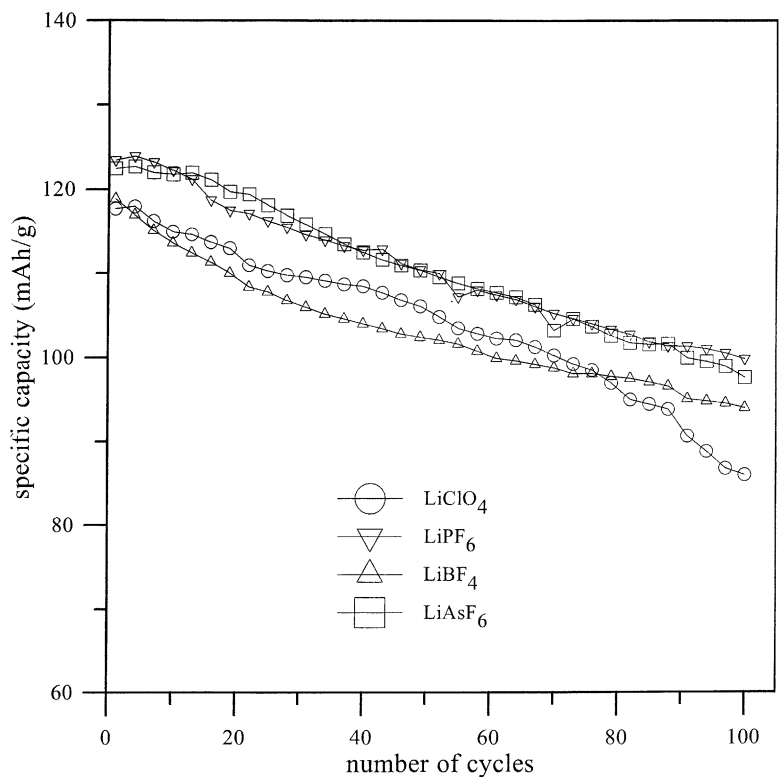
Fig. 9. Voltage–time profiles of Li/Li$_{1.05}$Mn$_2$O$_4$ cells with electrolyte solution 1 m LiClO$_4$ and LiBF$_4$ in PC 50.7%–DEC 49.3% (temperature 25 °C).

Fig. 10. Cyclability of specific capacity for Li/Li$_{1.05}$Mn$_2$O$_4$ cells with electrolyte solutions 1 m salt in PC 50.7%–DEC 49.3% (temperature 25 °C).

$\kappa_{(max)}$ values are increased, as is expected. As one can see from both Figs. 4 and 5, the difference between $\kappa_{(max)}$ of LiAsF$_6$ and LiPF$_6$ is not very significant, but it is between LiAsF$_6$ or LiPF$_6$ and LiClO$_4$ as well as between LiClO$_4$ and LiBF$_4$. This is in agreement with what was found by others, too [15,23].

The higher conductivities of LiAsF$_6$ and LiPF$_6$ can be explained with the larger anion radius of these salts, compared with that of LiClO$_4$ and LiBF$_4$, which means that the ionic dissociation ability of LiAsF$_6$ and LiPF$_6$ is higher than that of LiClO$_4$ and LiBF$_4$ as the coulombic force between Li$^+$ and the anion is weaker for larger radii [6].

Analogous behavior can be observed in Fig. 6, where the dependence of specific conductance on solvent composition for $m = 1\,mol\,kg^{-1}$ at 25 °C is presented. The values of the specific conductance for $m = 1$ were taken by intrapolating the experimental data. For LiAsF$_6$, LiPF$_6$ and LiClO$_4$ maxima are observed, whereas there are no data for LiBF$_4$ at PC 90.2%, so a conclusion cannot be drawn for this salt. The presence of the observing maxima is in accordance with the theory that the combination of a high dielectric constant liquid, which enforces the ionic dissociation, with a low viscosity liquid, that helps the ion migration, increases the conductivity [24]. Ion migration seems to be more effective for LiAsF$_6$ and LiPF$_6$, where the dissociation ability is higher, as the maxima for these salts are shifted to the left with respect to LiClO$_4$.

In Fig. 7 the dependence of the concentration, which corresponds to the maximum specific conductance, μ, on solvent composition, at 25 °C is given. All the salts seem to follow a concave up exponential trend. That means that μ is more sensitive in solutions poorer in PC.

The voltage time profiles of three typical circles for the four salts (1 m in PC 50.7%–DEC 49.3%) are presented in Figs. 8 and 9. The cells were first activated by charging up to 4.3 V and then cycled between 3.5 and 4.3 V. As it can be seen, all the salts show the same behavior. Two plateaus are observed at about 3.95 and 4.1 V, both in charge and discharge area, which correspond to the reversible electrochemical insertion and extraction of Li in spinel and to the change from one cubic phase to another with different lattice parameters [25,26].

In Fig. 10 the variation of the specific discharge capacity with the cycle number for Li/LiX in PC 50.7%–DEC 49.3% (1 m)/Li$_{1.05}$MnO$_4$ cells can be seen, where X represents the anion of the four studying salts. The obtained specific discharge capacity for the first cycle varied between 118 and 124 mAh g^{-1}, values which are about 80–84% of the theoretical one, 148.2 mAh g^{-1} [3] and usual for similar systems [4,25,27]. In all cases a similar decrease of about 20% in the specific discharge capacity was observed after 100 cycles. The capacity loss could be correlated with the dissolution of the spinel in the electrolyte solution [27].

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