

A study in conductances and physical constants of LiBF_4 + propylene carbonate–diethyl carbonate system

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Abstract

Viscosities and relative permittivities in the entire range of propylene carbonate (PC)–diethyl carbonate (DEC) binary system were measured. The conductometric behavior of lithium tetrafluoroborate (LiBF_4) in the above system was also studied as well as the electrochemical stability of an electrolyte solution of LiBF_4 in PC–DEC (1:1 w/w). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Conductance; LiBF_4 ; Propylene carbonate; Diethyl carbonate

1. Introduction

Propylene carbonate (PC) is a colorless stable substance of wide liquid range and high relative permittivity [1], which is widely used for high-energy lithium batteries [2,3]. From the other side, diethyl carbonate (DEC) is a low viscosity liquid, which is used as cosolvent [4,5]. Lithium tetrafluoroborate (LiBF_4) has been reported many times [5–10] as an electrolyte for Li or Li ion galvanic systems, too.

The above substances are mentioned very often in battery applications, but the PC–DEC + LiBF_4 system has not been investigated until today. As electrolytic conductivity plays a very important role in a galvanic system and conductivity depends on viscosity or relative permittivity variations, great interest can be attached to the behavior of LiBF_4 in a solvent mixture containing the high relative permittivity PC with the low viscosity DEC. The purpose of this paper is to investigate the possibility of use the PC–DEC + LiBF_4 system as electrolyte solution in a Li cell. So, viscosities and relative permittivities of PC–DEC mixtures were measured, as well as the conductance of LiBF_4 in the entire range of PC–DEC mixtures. The electrochemical stability of the solution was also tested.

2. Experimental

Both PC (Aldrich, 99%) and DEC (Merck, < 99.9%) were treated by distillation and molecular sieves 4 Å. LiBF_4 (Aldrich, 99.999%) was used as received. All solutions were prepared by mass, in a glove box, under Argon

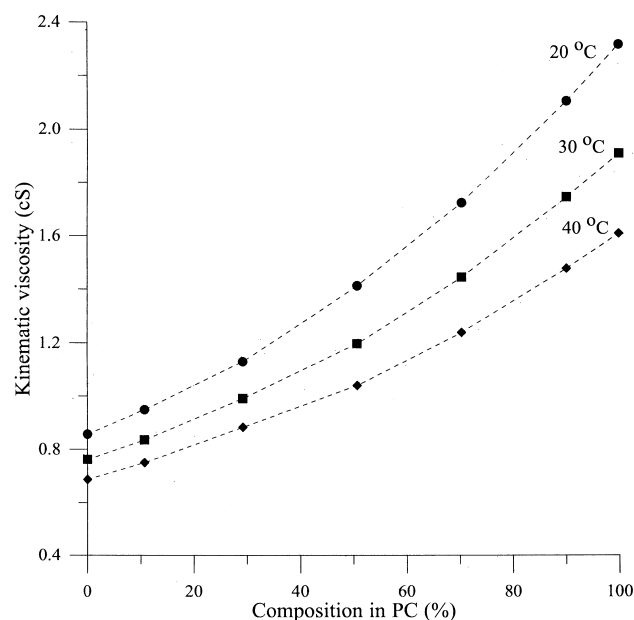


Fig. 1. Dependence of kinematic viscosity on composition of PC–DEC solvent mixture.

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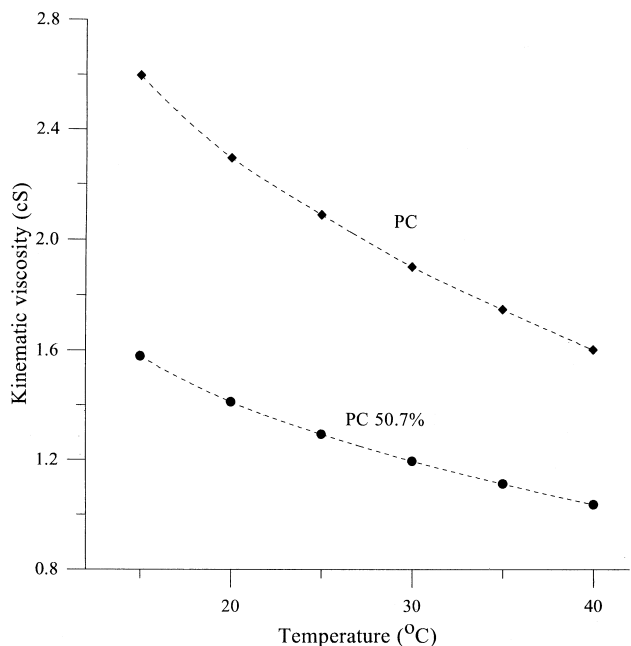


Fig. 2. Dependence of kinematic viscosity on temperature.

atmosphere, where humidity was lower than 2 ppm. A Shimadzu AEG-220 analytical balance of four decimal places was used for solution preparations. Glass cells used for conductance or cyclic voltammetry measurements were filled and tightly closed in the glove box. Water level in solutions before and after the experiments was approximately 50 ppm ($\pm 10\%$) (Karl–Fischer titration).

Kinematic viscosities were measured with an Ubbelohde suspended-level viscometer. Kinetic energy corrections were taken into account. Relative permittivity mea-

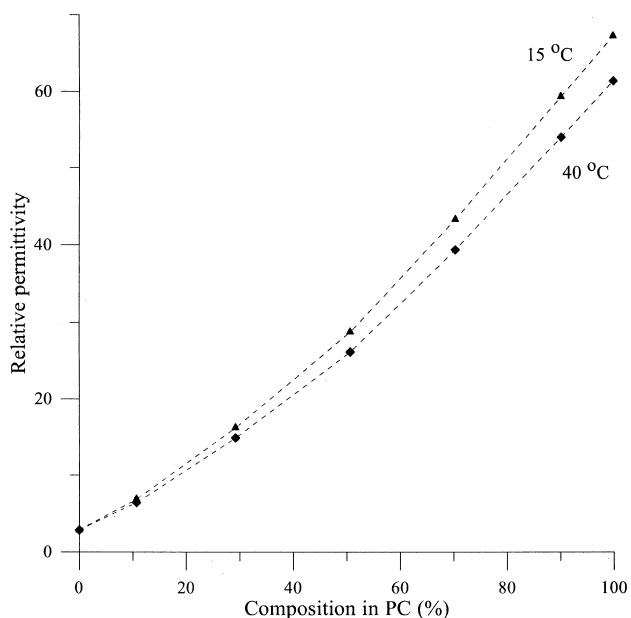


Fig. 3. Dependence of relative permittivity on composition of PC–DEC solvent mixture.

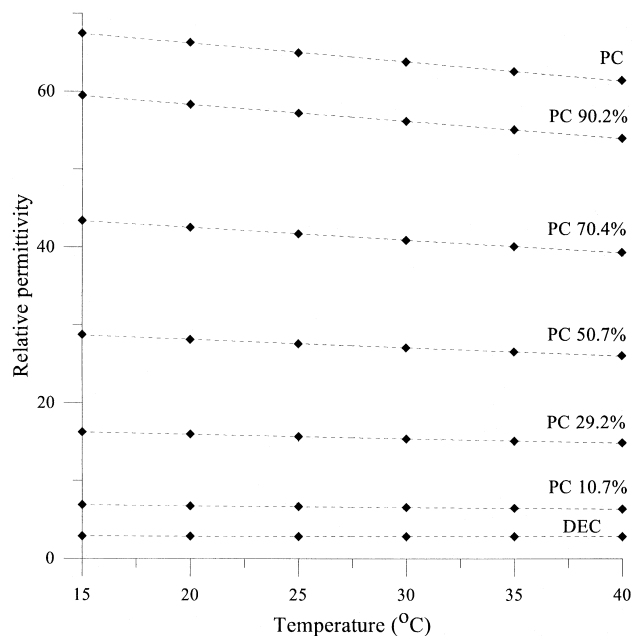


Fig. 4. Dependence of relative permittivity on temperature.

surements were made with a Wissenschaftlich Technische Werkstätten, model WTW DM-01, dipolemeter. Details about viscosity and relative permittivity measurements are given elsewhere [11,12].

Conductance measurements were made in glass cells, with platinized electrodes for minimizing polarization effects [13,14], calibrated with aqueous potassium chloride solutions. KCl preparation is described elsewhere [15]. The resistances of the solutions were measured using a Beckman (model RC-18A) conductivity bridge. Temperature in

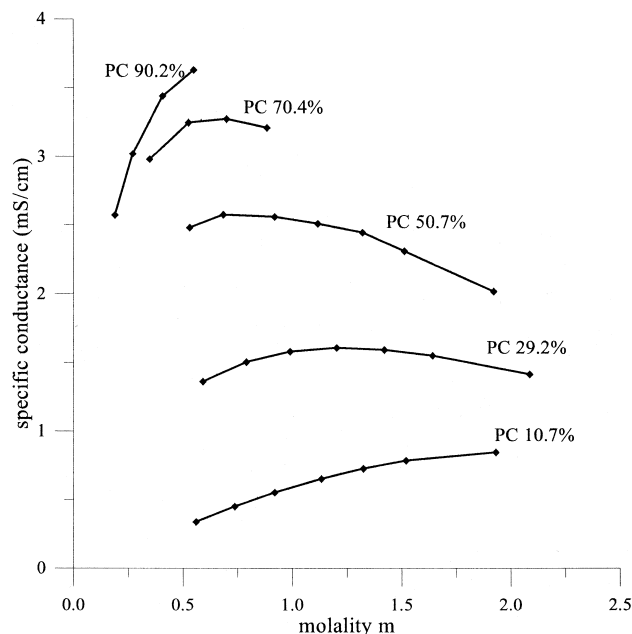


Fig. 5. Dependence of specific conductance on molality, for different compositions of $\text{LiBF}_4 + \text{PC-DEC}$ system, at 25°C.

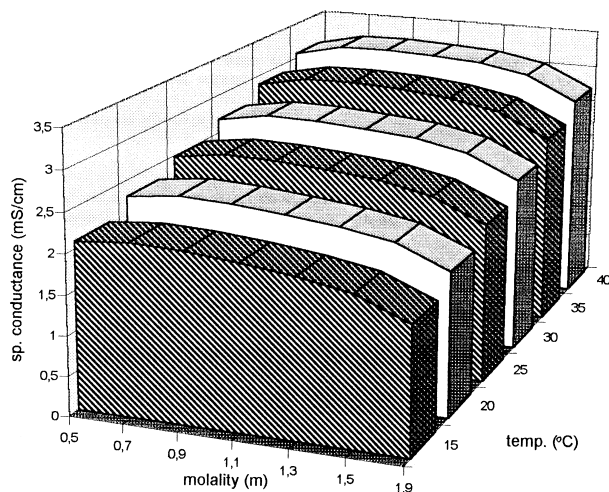


Fig. 6. Dependence of specific conductance on molality and temperature, for $\text{LiBF}_4 + \text{PC } 50.7\% - \text{DEC } 49.3\%$ system.

viscosity, relative permittivity and conductance measurements was regulated by a YSI (model 72) thermostat.

Cyclic voltammetric measurements were made by a Bank Elektronik Wenking Potentiostat POS 73 and a Linseis LY 1400 x–y recorder, in a three-type cell with Al working electrode and Li counter and reference. Li and Al metals (Aldrich) were used without pretreatment. The sweep rate was 100 mV/s.

3. Results and discussion

The PC composition in the mixtures was 90.2, 70.4, 50.7, 29.2 and 10.7% w/w. Variation of kinematic viscosity with PC composition is presented in Fig. 1, for 20°, 30° and 40°C. In all temperatures, on increasing the PC composition, kinematic viscosity increases normally, without maximum or minimum. Dependence of kinematic viscosity on temperature is given in Fig. 2, for PC and PC 50.7%–DEC 49.3% mixture. As is expected, on increasing the temperature, kinematic viscosity decreases.

The variation of relative permittivity with the composition of the mixture can be seen in Fig. 3, for 15° and 40°C. The values from 20° to 35°C lie normally between 15° and 40°C. The values at every temperature seem to follow a smoothing curve and have the same behavior with other studied mixtures of PC with organic solvents of low relative permittivity [16,17]. As can be seen in Fig. 4, the variation of relative permittivity with temperature is linear, in every composition. Temperature effect on relative permittivity is more obvious in mixtures rich in PC. This has also been observed in other similar systems [18].

LiBF_4 was not possible to be soluted, at room temperature, over ~ 1.2 m in PC 70.4%–DEC 29.6% mixture and over ~ 0.8 m in PC 90.2%–DEC 9.8% mixture. In the other mixtures, the conductivity was measured from 0.5 to 2 m. The specific conductance of the mixtures at 25°C is presented in Fig. 5, as a function of the concentration of

LiBF_4 . A maximum was observed in mixtures containing 29.2, 50.7 and 70.4% PC, lying at ~ 1.2 , 0.65–0.95 and 0.6–0.75 m, correspondingly. Mixture containing PC 10.7% seems to reach a possible maximum over ~ 1.8 m, whereas, it is not easy to get a conclusion for the mixture containing PC 90.2% with the existing data. The behavior in the other temperatures was analogous and, as is expected, on increasing the temperature, the conductance increases, which can be attributed to the decrease of the viscosity. Dependence of specific conductance on temperature and molality is given in Fig. 6, for PC 50.7%–DEC 49.3% mixture.

Since an electrolyte solution which will be used in a battery has to be electrochemically stable at least up to the charge voltage of the cell, we measured by cyclic voltammetry the electrochemical stability of a solution containing ~ 0.65 m LiBF_4 in PC 50.7%–DEC 49.3%. As Al is usually used as current collector in Li cells, it was chosen as working electrode. The voltammogram was flat between 2 and 5 V, thus indicating that there is no measurable oxidation of the solution in this voltage range. The performance of a Li cell using this electrolyte solution and $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ as cathode material will be investigated in the future.

Acknowledgements

This work was financially supported partly by the Greek General Secretariat of Research and Technology, Ministry of Development, under the project ‘ENVIBAT/664’ in collaboration with ‘Germanos Batteries’.

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