

## A Study of Electrochemical Kinetics of Lithium Ion in Organic Electrolytes

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**Abstract**—Limiting current densities equivalent to the transport-controlling step of lithium ions in organic electrolytes were measured by using a rotating disk electrode (RDE). The diffusion coefficients of lithium ion in the electrolyte of PC/LiClO<sub>4</sub>, EC : DEC/LiPF<sub>6</sub> and EC : DMC/LiPF<sub>6</sub> were determined by the limiting current density data according to the Levich equation. The diffusion coefficients increased in the order of PC/LiClO<sub>4</sub> < EC : DEC/LiPF<sub>6</sub> < EC : DMC/LiPF<sub>6</sub> with respect to molar concentration of lithium salt. The maximum value of diffusivity was  $1.39 \times 10^{-5} \text{ cm}^2/\text{s}$  for 1 M LiPF<sub>6</sub> in EC : DMC = 1 : 1. Exchange current densities and transfer coefficients of each electrolyte were determined according to the Butler-Volmer equation.

Key words: Lithium Ion Batteries, RDE, Electrolyte, Limiting Current Density, Diffusion Coefficient

### INTRODUCTION

In the last decade many studies have been performed to develop secondary lithium batteries [Blomgren, 1993; Dominey, 1994; Nam et al., 2001]. Recent development and applications of lithium ion batteries (LIB), of which the anode is a carbon-lithium intercalation compound and the cathode is lithiated metal oxide, are being commercialized rapidly. Despite significant achievements in LIB, mass transport data of lithium ion in bulk phase of the organic electrolytes are limited as compared with the practical aspects of researches such as development of the electrode materials, enhancement of the cycle efficiency [Langenhuizen, 1998]. In particular, basic data for ethylene carbonate (EC)-based mixed electrolytes are insufficient, in spite of the fact that EC-electrolyte systems are applied to commercial lithium ion batteries. The mass transport of lithium ion in the electrolytes gives an effect on the performance of batteries, because lithium ion batteries have porous electrodes and a separator to be immersed in the electrolyte. Therefore, it is necessary to obtain data of the transfer properties (viscosity and mass diffusivity) of lithium ions in organic electrolytes and the kinetic parameters for the optimal design of lithium batteries.

Propylene carbonate (PC), which forms a stable protective insulating layer-solid electrolyte interphase (SEI) on lithium electrode, has been applied to lithium primary batteries [Blomgren, 1993]. Therefore, the basic data of PC-based electrolytes have been well established. But lithium secondary batteries demand more complex functions of SEI with carbon electrode. Recent results show that EC-based electrolyte systems are suitable to LIB because these are more highly conductive and slightly lower viscous than PC-systems and exhibit good SEI characteristics with carbon anode. Many studies are reported focusing on the high ionic conductivity or interface analysis for various EC-based mixed solvent electrolyte systems with various compositions [Ishikawa et al., 1994; Naoi et al., 1996; Zhang et al., 1996; Kanamura et al., 1997]. Specially,

Ein-Eli et al. [1996, 1997] and Aurbach et al. [1995, 1996] have published a series of considerable researches about the passive film of lithium batteries in different organic electrolytes.

Since high permittivity solvents (HPS) such as PC and EC have a high viscosity that hinders the mass transport of solutes, these solvents are mixed with low viscosity solvents (LVS) such as dimethoxy ethane (DME), dimethyl carbonate (DMC), diethyl carbonate (DEC) [Matsuda et al., 1986]. This is because the solid phase of EC at room temperature EC is usually blended with these solvents. As the solute providing lithium ion, inorganic salts such as LiPF<sub>6</sub>, LiAsF<sub>6</sub>, etc. are mainly used, lithium perchlorate tends not to be used for commercial batteries but in the laboratory.

The aim of this experiment was to investigate the mass transfer properties of lithium ion in organic electrolyte for secondary lithium batteries by finding limiting current densities of electrodeposition of lithium ( $\text{Li}^+ + \text{e}^- \Rightarrow \text{Li}$ ) on the rotating disk electrode (RDE), which is suitable for studying the mass transport of a salt in electrolytes [Quickenden and Jiang, 1984; Uceda et al., 1990; Lee et al., 2000]. In addition, electrochemical parameters such as exchange current density and electrochemical transfer coefficient of each electrolyte were determined according to the Butler-Volmer equation.

### EXPERIMENTAL

Propylene carbonate (PC, Aldrich, 99%), ethylene carbonate (EC, Aldrich, 99%), diethyl carbonate (DEC, Aldrich, 99%), and dimethyl carbonate (DMC, Aldrich, 99%) were used for solvent of electrolytes. These organic solvents were distilled under reduced pressure prior to use. LiClO<sub>4</sub> (Aldrich, 99.99%) was dried at 120 °C for 24 h under vacuum and LiPF<sub>6</sub> (Aldrich, 99.99%) was used as received. The following electrolytes for electrochemical tests were prepared:

0.1, 0.5, 0.75, 1.0 M LiClO<sub>4</sub> in PC (PC/xM LiClO<sub>4</sub>)

0.1, 0.5, 0.75, 1.0 M LiPF<sub>6</sub> in 1 : 1 mixture (wt%) of EC and DEC (EC : DEC = 1 : 1/xM LiPF<sub>6</sub>)

0.1, 0.5, 0.75, 1.0 M LiPF<sub>6</sub> in 1 : 1 mixture (wt%) of EC and DMC (EC : DMC = 1 : 1/xM LiPF<sub>6</sub>)

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