



# Enhancement of Li<sup>+</sup> ions mobility on activated carbon electrode for lithium ion capacitor



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## ARTICLE INFO

### Article history:

Received 11 November 2016

Received in revised form 22 February 2017

Accepted 27 February 2017

Available online 6 March 2017

### Keywords:

THF  
electrolyte  
lithium ion capacitor  
capacitive resistance  
ion mobility

## ABSTRACT

As an electrolyte solvent for lithium ion capacitors (LICs), tetrahydrofuran (THF) showed lots of advantages on increasing the discharge capacity, suppressing the potential drop at charged state, and improving the slope of discharge curve. Several electrochemical studies were conducted to verify these effects of THF on LICs. The open circuit potentials of AC/Li beaker-cells with THF were shifted to more positive potentials because of the lowered electrostatic potential of the electrolyte, the weakened solvation energy with LiBF<sub>4</sub>, and the easier adsorption of BF<sub>4</sub><sup>-</sup> ions to AC electrode in aging step. Although the concentration of LiBF<sub>4</sub> decreased with adding THF, the electrolyte conductivity increased by the improved mobility of ions more than enough to compensate to the electrolyte conductivity decreasing by the reduced salt concentration. The capacitive resistance of activated carbon (AC)/Li cell was little changed by adding THF in fully charged state but was much smaller in fully discharged state than the reference condition. These results imply that THF seldom disturbed the behavior of BF<sub>4</sub><sup>-</sup> ions but accelerated the mobility of Li<sup>+</sup> ions at AC electrode.

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## 1. Introduction

In the field of electrical energy storages large scale devices have recently been attracted attention for electric vehicles or wind and solar powered energy storage systems. These applications require higher power performances than the energy storages for small electric tools, such as cellular phones and notebooks [1]. Of the technologies being developed for these high-power energy storage devices, lithium ion capacitor (LIC) is one of the possible candidates [2,3]. The LIC is a hybrid system comprised of graphite electrode of lithium ion batteries (LIBs) as anode and activated carbon (AC) electrode of supercapacitors (SCs) as cathode. Therefore, LICs can produce higher power densities than LIBs and larger energy densities than SCs [4].

However, the research on the electrolyte for LICs has not been reported so much. Especially, much remains to research on the interface at AC electrode because the electrolytes for LICs were designed to fit only the graphite electrode being worked by Faradaic reaction of Li<sup>+</sup> ions. Even on the electrolyte research for AC electrode being worked by non-Faradaic reaction of ions, the electrochemical behaviors of aqueous electrolytes have been

reported much more than organic electrolytes [5,6]. Even within the field of organic electrolytes for AC electrode, extensive studies have focused on the electrolyte with some quaternary ammonium or phosphonium tetrafluoroborate, which have not used for LIBs [7].

We have reported on the electrochemical behavior of the electrolyte components in SCs or LICs from a few years ago, such as the effect of electronic spatial extents (ESE) of ions on overpotential of AC electrode in charging and discharging steps and 1,3,5-Trifluorobenzene (TFB) as an electrolyte additive to improve the performance of LICs [8,9]. These results were effective on designing the electrolyte that could decrease the resistance at AC electrode and finally could improve high-rate discharge performances of LICs.

In this research, we report experimental results on tetrahydrofuran (THF) as an electrolyte component for LICs. The research motivation was that the electrolyte conductivity increased by THF addition and the open circuit potentials (OCPs) of AC/Li cells shifted to more positive potentials. Even though THF has been considered as an electrolyte solvent for various electrochemical cells due to its low viscosity, there is not much applications owing to its low oxidation potential relatively and low boiling point [10–13]. On the other hand, because LICs have lower operating voltage range of 4.0 to 2.0V than LIBs, THF can be used as an electrolyte solvent for LICs if the effect of THF has been verified on

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highly porous AC electrode. In the present work we evaluate and discuss the working mechanism of THF as an electrolyte component of LICs *via* basic electrochemical analyses such as electrolyte conductivity, initial OCP in aging step, linear sweep voltammogram (LSV), rate-discharge curve and electrochemical impedance spectroscopy (EIS) of home-made AC/Li cell.

## 2. Experimental

All experiments were performed using a mass produced AC electrode, which was obtained from Korea JCC Co. Electrodes were dried for a day at 80 °C in a vacuum oven prior to experiments. The reference electrolyte was ethylene carbonate/diethyl carbonate (EC/DEC=3/7, vol%) containing 1.0 M LiBF<sub>4</sub>, which was obtained from Soulbrain Co., Korea. THF was purchased from Enchem Co. and stored with molecular sieve for several days before use. The electrolytes for this study were designed by mixing THF with the reference electrolyte on a weight basis in humidity controlled (<10 ppm) glove box filled with argon. The conductivity of the electrolytes was measured using a portable conductivity meter (EC-400L; Istek Inc.). LSV was measured using a beaker cell with three electrodes, a platinum (Pt) electrode (working electrode), and two Li metal sheets (reference and counter electrodes). The OCPs of AC/Li beaker-cells composing of microporous AC (working electrode) and two Li metal sheets (reference and counter electrodes) were checked for 30 min after added THF into the electrolyte. To measure the electrochemical properties of THF as an electrolyte component, home-made AC/Li cells were designed using Li metal electrode (3.0 × 3.5 cm) and AC electrode (2.5 × 2.5 cm). All AC/Li cells were assembled in a glove box, using a microporous AC electrode, a Celgard (2320) separator, and Li metal. Other details for the cell fabrication were as previously described [14]. AC/Li cells were charged from their OCPs to 4.0 V at 1.0C (1.0C=1.8 mA), subjected to constant potential (4.0 V vs (Li/Li<sup>+</sup>)) until 0.1C capacity drop (CC-CV charging) was observed, then discharged to 2.0 V at different rates (CC discharging). AC/Li cells were charged from their OCPs to 4.0 V at 1.0C (1.0C=1.8 mA), subjected to constant voltage (4.0 V) until 0.1C capacity drop (CC-CV charging) was observed, then discharged to 2.0 V at different rates (CC discharging). The EIS measurement of AC/Li cells was performed using an IM-6ex (Zahner Elektrik) at frequencies varying from 1 MHz to 10 mHz and an amplitude of 10 mV. EIS data was analyzed using Zman fitting software (Ver. 2.2, Scribner Associates, Inc.). To obtain reliable EIS data, AC/Li cells were fully charged to 4.0 V or discharged to 2.0 V, and all cell tests were conducted in a temperature-controlled (20 °C) chamber.

## 3. Results and discussion

### 3.1. THF effect on electrolyte conductivity and linear sweep voltammograms

Fig. 1 shows the ionic conductivity of the electrolyte with a concentration of THF. Since the electrolytes for this study were designed by mixing THF with the reference electrolyte on a weight basis, the salt concentration decreased with THF but the electrolyte conductivity increased to 20 wt% THF and then decreased. Generally, the ionic conductivity is related to the movement of anions and cations, depending on each ion's quantity,  $C_i$ , and mobility,  $u_i$ . The electrical mobility of ions is related to the viscosity,  $\eta$ , of the electrolyte as described by Eqs. (1)–(3) [10].

$$\kappa = F \sum |z_i| u_i C_i \quad (1)$$

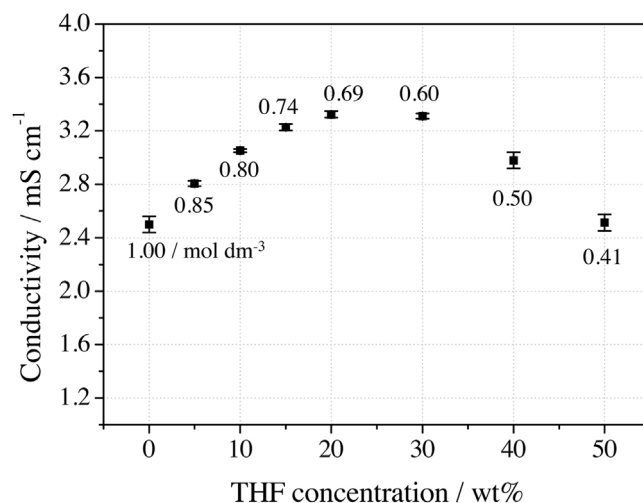


Fig. 1. Electrolyte conductivity with a concentration of THF measured at 20 °C. Inserted numbers are the concentration of LiBF<sub>4</sub>.

$$u_i = \frac{1}{6\pi\eta r_i} \quad (2)$$

$$\eta_{mixture} = \eta_i^{1-x} \eta_j^x \quad (3)$$

The factors of charge ( $z_i$ ) and radius ( $r_i$ ) for each ion are not changed by adding THF. Therefore, the experimental results indicate that the ionic conductivity increased due to the improved mobility of each ion in the electrolyte, which was induced from the decreased viscosity by adding THF.

Since the ratio of LiBF<sub>4</sub> and EC is not changed by adding THF, on the other hand, the solvated structure of LiBF<sub>4</sub> with EC can maintain even after added THF because the dielectric constant of THF (7.58) is much smaller than EC (89). However, the salt concentration of the electrolyte is changed with charging depth in AC/Li cell. In charged state, for example, BF<sub>4</sub><sup>-</sup> ions are adsorbed at AC electrode and Li<sup>+</sup> ions are reduced at Li metal electrode. Therefore, the salt concentration is got to be lower state and the content of free EC is higher state in electrolyte. In discharged state, by contrast, BF<sub>4</sub><sup>-</sup> ions are desorbed from AC electrode and Li<sup>+</sup> ions are oxidized from Li metal electrode. Therefore, the concentration of each ion is higher state and the content of free EC is lower state in electrolyte. Because the dielectric constant of THF is much smaller than EC but a little larger than DEC (2.8), on the other hand, THF addition to the electrolyte can have a positive effect to increase the transport velocity of each ion in discharged state, not only by decreasing the electrolyte viscosity but also by reducing the solvation energy with LiBF<sub>4</sub>. Based on these experimental results on the conductivity, the electrochemical properties of AC/Li cell with the electrolyte containing 15.0 wt% THF were analyzed intensively.

Fig. 2 shows the LSV data for the electrolyte with or without THF measured on Pt electrode. A reduction peak at 1.8 V for the reference electrolyte represents the decomposition of EC solvated with LiBF<sub>4</sub> [15]. This reduction peak was shifted slightly to more positive potential on the electrolyte containing THF. Since THF is not easy to solvate with LiBF<sub>4</sub> than EC and is difficult to be reduced at more positive potential than -2.0 V vs (Li/Li<sup>+</sup>) as reported [11], we concluded that this peak shift was induced by the electrolyte conductivity increased by adding THF.

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