Electrochimica Acta 131 (2014) 240–244

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Influence of the electrolyte distribution near the micropores of the activated carbon (AC) electrode on high rate performance of high voltage capacitors

Chung ho Lee, Fan Xu, Cheolsoo Jung*

Department of Chemical Engineering, University of Seoul, 163 Shiripdaero, Dongdaemun-gu, Seoul, 130-743, Republic of Korea

ARTICLE INFO

Article history:
Received 14 September 2013
Received in revised form 17 February 2014
Accepted 17 February 2014
Available online 3 March 2014

Keywords:
1,3,5-Trifluorobenzene
Capacitor
Overpotential
Anion adsorption
Electrolyte distribution

ABSTRACT

This paper presents a method to enhance the rate performance of high voltage capacitors using an electrolyte additive, 1,3,5-trifluorobenzene (TFB). With increasing discharge rate, the capacity of the activated carbon (AC)/lithium (Li) cell decreases with increasing the slope of the discharge curve and its potential drop at 4.6 V. By adding TFB, the discharge slope improves to increase the rate performance of the cell, and EIS showed that the charge transfer resistance (Rc) of the AC cell decreases. These results suggest that TFB affects the distribution of the electrolyte components near the microporous AC and improves the rate performance of the AC cell.

1. Introduction

Lithium ion capacitors (LICs) are a type of hybrid capacitor that uses Li^+ intercalation in a graphite anode to improve the low energy density of electric double layer capacitors (EDLCs) [1–3]. On the other hand, to broaden the utility of LICs, they must be designed with sufficient energy density to serve as substitutes for Li ion batteries. Many methods have been proposed to increase the energy density of microporous activated carbon (AC) electrodes, such as increasing the surface area [4,5], improving the operating potential [3,6,7], modifying surfaces [8], and enhancing the high-rate performance [9–11]. The relationship between the ion and pore size has also been studied for EDLCs [12]. For maximum double-layer capacitance, the ion size in the electrolyte should be close to the pore size. Nevertheless, the overpotential during high rate operation has not been examined in detail. Recently, V. Khomenko et al. reported LICs with an operating potential ranging from 1.5 V to 4.5 V, but they did not show the experimental results obtained under high rate conditions [3]. An aqueous hybrid electrochemical capacitor with 4.2 V was also reported using a polymeric coated Li metal electrode [6]. On the other hand, performance degradation under high rate conditions still occurred, even with the use of an aqueous electrolyte. As mentioned previously, it is difficult to increase the energy or power density of the capacitor series by increasing the operation voltage.

This paper reports a novel method to enhance the rate performance of high voltage capacitors using an electrolyte additive. As studied previously, the electrolyte additive, such as 1,3,5-trifluorobenzene (TFB), can lower the transfer energy of Li^+ ions on the electrode surface, such as a $LiCoO_2$ electrode [13]. This effect is believed to be due to its structural identity, a locally biased polar structure. Because of its mere biased polarity, TFB can alter the electrode potential and open circuit potential (OCP) by rearranging the electrolyte components near the electrode surface. When TFB was added, the OCP of a $LiCoO_2$ half-cell shifted to a slightly higher positive direction, which can affect the electrolyte distribution near the $LiCoO_2$ electrode. Owing to these changes in the electrolyte near the cathode electrode, the cell with TFB had better discharge properties, even under high rate conditions, compared to a half-cell without TFB. This mechanism for the electrolyte distribution near the positive electrode of the Li ion battery could be applied to a microporous AC electrode, which is a representative positive electrode of the capacitor series. In this study, TFB improved the capacitor performance, and the experimental results were verified by analyzing the potential drop, slope of the discharge curve, and impedance component.

---

* Corresponding author. Tel.: +82-2-6490-2368; fax: +82-2-6490-2364.
E-mail address: csjung@uos.ac.kr (C. Jung).

http://dx.doi.org/10.1016/j.electacta.2014.02.093
0013-4686/© 2014 Elsevier Ltd. All rights reserved.

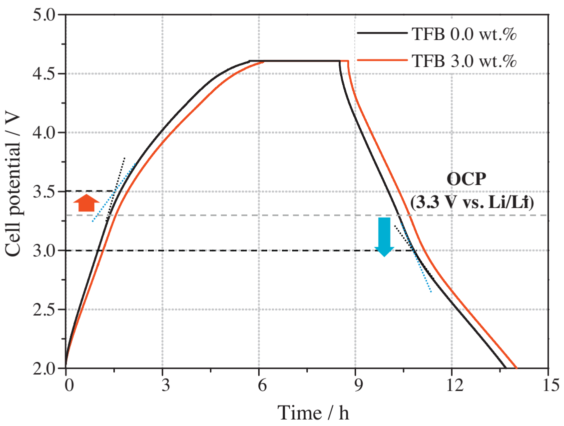

Fig. 1. Continuous profile of the charge and discharge of microporous AC/Li cells with 1.0 M $LiBF_4$ in EC/DEC (= 3/7, v/v%) depending on TFB addition. 0.2 C charge to 4.6 V and CV to a 0.1 C capacity drop, 0.2 C discharge to 2.0 V.

2. Experimental

All experiments were performed using homemade pouch AC/Li cells composed of a Li metal electrode with a larger area (3.0 cm × 3.5 cm) than the AC electrode (2.5 cm × 2.5 cm). All the cells were composed of a microporous AC, separator and Li metal. A mass production grade microporous AC electrode was received from Korea JCC Co. Each electrode was dried for 24 h at 80 °C in a vacuum oven prior to cell fabrication. Celgard (2320) was used as the separator, and Li metal was used as the counter electrode for the full cells. The basic electrolyte composition was ethylene carbonate/diethyl carbonate (EC/DEC = 3/7, v/v%) with 1.0 M $LiBF_4$, which was obtained from Soulbrain Co. 1,3,5-trifluorobenzene (TFB), was purchased from Sigma Aldrich Korea Co. and used as received. The entire cells were assembled in a humidity controlled (<10 ppm) glove box filled with argon gas. All the fabricated cells were prepared using the reported method [13]. The AC/Li cells were charged from the open circuit potential (OCP) to 4.6 V at a 0.2 C (1.0 C = 5.7 mA) rate, followed by a constant voltage (4.6 V) to a 0.1 C capacity drop (CC-CV charging), and were discharged to 2.0 V or 3.0 V at various rates (CC discharging). The impedance of the AC/Li cell was analyzed using IM-6ex (Zahner Elektrik), whose frequency was varied from 3 MHz to 10 mHz, and the amplitude was set to 5 mV. The electrochemical impedance spectroscopy (EIS) data was analyzed using Zman 2.0 software. All the EIS data was obtained from the fully charged cells to 4.6 V at 0.2 C. The entire cell tests were operated in a temperature-controlled (i.e. 20 °C) chamber.

3. Results and discussion

3.1. Charge and discharge curve of the AC/Li cell

Fig. 1 shows the continuous charge and discharge profile of the microporous AC/Li cell. The arrows mean a shift of the inflection points from OCP of the cell in the discharge (aqua arrow) and charge state (red one). The cell was charged to 4.6 V, which is a relatively higher voltage than that of reported capacitors including Li ion capacitors, and then discharged to 2.0 V at 0.2 C rate. Generally, EDLCs have an almost straight slope for the charge and discharge processes because EDLCs are composed of two symmetrical AC electrodes, which each voltage is sustained by one type of ion [14]. On the other hand, the charge and discharge profiles were not straight because the AC/Li cell is not a symmetrical cell and its voltage changes depending mainly on the electron density of ions that are adsorbing or desorbing into the microporous AC electrode. During their charging and discharging, the potential of the Li metal electrode maintained almost 0 V (vs. Li/Li^+) with standard deviation of ± 20 mV. Because this is a negligible value compared to the potential change in the AC electrode, the voltage change with charging and discharging of the cell is believed to be induced by the potential change of the AC electrode. The OCP of a pristine AC electrode was almost 3.3 V in EC/DEC (= 3/7, v/v%) with 1.0 M $LiBF_4$ after aging the cell for 5 hrs. The OCP means the electrostatic potential of the AC electrode, which is affected by adsorbing the electrolyte components, such as ions, solvents and additives. In contrast to the OCP of the $LiCoO_2$/Li cell in the previous report [13], the OCP of the AC/Li cell changed little by adding TFB. This is not a strange result, inducible from a different working electrode. These results suggest that BF_4^- ions are desorbed from the AC interphase over 3.3 V and Li^+ ions are adsorbed under 3.3 V in the discharging process of the AC/Li cell.

As shown in Fig. 1, the slope was changed over 3.5 V in the charge process (red arrow) and under 3.0 V in the discharge process (blue arrow). These results suggest that the overpotentials can be formed easily in the desorption process of Li^+ ions during charging and of BF_4^- ion during discharging, particularly under high-rate operating condition. Another noticeable point is that the discharging time of the cell was increased slightly by adding TFB. Because the discharging time is affected by the adsorbing BF_4^- ions, these experimental results indicate that TFB can help BF_4^- ions desorb to a microporous AC electrode, even at a low discharge rate, 0.2 C. On the other hand, by inserting the constant voltage (CV) step at 4.6 V to maintain the same charged state, the discharge slope and discharging time were not changed by the addition of TFB.

3.2. TFB effect on the discharge curve of AC/Li cells

The rate-discharge capacities of AC/Li cells were compared to discuss the effects of the electrolyte additive, TFB, on the microporous AC electrode. As shown in Fig. 2 (a), the discharge capacity of the cell was increased by adding TFB, particularly under high rate conditions. The capacity of the cell without TFB was 2.66 mAh at 10.0 C, which was only 47% of the capacity at 0.2 C. On the other hand, the capacity of the cell with 3.0 wt.% TFB was 3.37 mAh at 10.0 C, which was 58% of its 0.2 C condition. To explain why TFB increases the capacity at high rates, the discharge curves were compared as a function of the capacity, as shown in Fig. 2(b). The discharge capacity decreased with increasing potential drop and its slope on the higher discharge rate condition. In addition, this performance degradation was prevented by adding TFB to some degree clearly.

3.3. TFB effect on the potential drop of the discharge curve

To determine the prevention mechanism of the performance degradation by TFB addition, the extent of the potential drop on the discharge rate was calculated from 4.6 V after charging on 0.2 C. As shown in Fig. 3, the potential drop increased with increasing discharge rate but its difference showed little change by adding TFB. Generally, this type of potential drop is referred to as the overpotential-induced IR drop, and typically increases with increasing discharge rate [15] or electrolyte resistance [16]. These results show that the potential drop increased with increasing discharge rate but the concept of the electrolyte resistance did not match this research condition. Although the conductivity of the electrolyte decreased from 1.68 to 1.55 mS/cm^2 by adding TFB, their mean potential drops were similar but the capacity of the cell increased, as shown in Fig. 3. This is a very encouraging result because this type of potential drop is one of the major causes of performance degradation in microporous capacitors [17].