Short Communication

Li(CF$_3$SO$_2$)$_2$N as an electrolytic salt for rechargeable lithium batteries with graphitized mesocarbon microbeads anodes

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Abstract

The suitability of Li(CF$_3$SO$_2$)$_2$N, lithium bistrifluoromethylsulfonyl imide, as an electrolytic salt for a graphitized mesocarbon microbeads (MCMBs) anode is investigated via charge/discharge cycling tests and a.c. impedance spectroscopy. The application of Li(CF$_3$SO$_2$)$_2$N resulted in excellent discharge (corresponding to the de-intercalation of lithium ion from MCMBs) capacity and stable charge/discharge cycleability of the anode in a 1:1 mixture (by volume) of ethylene carbonate with dimethyl carbonate or diethyl carbonate. According to the a.c. impedance analysis, the Li(CF$_3$SO$_2$)$_2$N electrolyte systems maintained a stable interfacial resistance between the anode and the electrolytes during charging of the anode.

Keywords: Lithium imide; Carbon anodes; Mesocarbon microbeads; Rechargeable lithium batteries

1. Introduction

It is widely known that lithium salts as electrolytic salts affect the performance of both lithium-ion and lithium–metal batteries. These performance parameters include charge/discharge characteristics, internal resistance, and electric/thermal stability. Lithium hexafluorophosphate (LiPF$_6$) has been typically used as the electrolytic salt in lithium-ion batteries. This is because it provides relatively high discharge (corresponding to the de-intercalation of lithium) capacity of carbon material anodes and shows high conductivity that offers low-internal resistance and high-rate charge/discharge performance cells [1]. Unfortunately, however, LiPF$_6$ is not sufficiently stable and is sensitive to moisture in the electrolyte. We have reported previously [2] that lithium trifluoromethanesulfate (LiCF$_3$SO$_3$) has excellent suitability for carbon fibre anodes with graphite structure. Throughout charge/discharge cycling of carbon fibre anodes, LiCF$_3$SO$_3$ was found to offer a more stable and higher discharge capacity of the carbon fibre than LiPF$_6$ under our experimental conditions. A shortcoming of solvent systems that contain LiCF$_3$SO$_3$ is poor conductivity which is below half that of corresponding solvent systems containing LiPF$_6$ [2]. This

drawback would limit the extensive application of LiCF$_3$SO$_3$ to the electrolytic salt in practical lithium battery systems.

Recently, considerable interest has been focused on lithium bistrifluoromethylsulfonyl imide, Li(CF$_3$SO$_2$)$_2$N, as an alternative lithium salt for lithium batteries. This is because electrolytes containing Li(CF$_3$SO$_2$)$_2$N display high conductivity that is equivalent to that of LiPF$_6$ electrolyte systems. Moreover, Li(CF$_3$SO$_2$)$_2$N has good stability comparable with LiCF$_3$SO$_3$ [3,4].

To date, little is known about the suitability of Li(CF$_3$SO$_2$)$_2$N for carbon anodes with highly graphitized structures [5]. There have been reports, however, on the fundamental chemical and physical properties of Li(CF$_3$SO$_2$)$_2$N and some attempts have been made to apply it to lithium battery systems with disordered carbon or lithium metal anodes [3–7]. This study examines the suitability of Li(CF$_3$SO$_2$)$_2$N for a mesocarbon microbeads (MCMBs) anode with a highly graphitized structure formed by heat-treatment at 2800 °C. Charge/discharge cycling tests of the MCMBs anode and a.c. impedance measurements during charging have been performed in a 1:1 mixture (by volume) of ethylene carbonate (EC) with dimethyl carbonate (DMC) or diethyl carbonate (DEC) with Li(CF$_3$SO$_2$)$_2$N as the electrolytic salt. These mixed solvent systems, EC–DMC and EC–DEC, have been extensively used for typical rechargeable lithium batteries with carbon anodes.

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2. Experimental

Li(CF$_3$SO$_2$)$_2$N was provided by Sumitomo 3M and was vacuum dried at 110 °C. The organic solvents were EC, DMC, and DEC (Mitsubishi Chemical, Battery Grade). The electrolytes were 1 M solutions of the lithium salt dissolved in a 1:1 mixture (by volume) of EC with DMC or DEC. These mixed solvents are expressed as EC–DMC and EC–DEC, respectively.

The MCMBs were prepared from coal-tar pitch by the Osaka Gas Company. The beads were separated and then washed. After drying, the beads were classified to give a particle size of ~6 μm in average diameter. The beads were then graphitized at a temperature of 2800 °C after carbonization at 1000 °C. The details of the MCMBs preparation have been described elsewhere [8–10]. The resulting MCMBs have a highly graphitized bulk; d_{002}, a_0, L_C, and L_a were 3.37, 2.46, 460, and 610 Å, respectively [10].

For the preparation of MCMBs anodes, the MCMBs were mixed with 5 wt.% poly(vinylidene fluoride) (PVDF) binder in 1-methyl-2-pyrrolidinone (NMP). The resulting slurry was spread uniformly on a disc of copper foil (~0.95 cm^2 in area). The NMP in the slurry was evaporated at 120 °C under reduced pressure for 24 h. Finally, the MCMBs-coated disc was dried at 80 °C under reduced pressure for 24 h. The average weight of MCMBs on the copper disc was ~15 mg.

The charge (intercalation of lithium ions into MCMBs)/ discharge (de-intercalation) cycling tests were performed using coin-type cells under a constant current. The test cells were constructed using 2032 coin cell hardware with the above MCMBs anode, a polypropylene separator, and a disc of lithium sheet (2.27 cm^2 in area and 0.24 mm in thickness) as a counter electrode, refer Fig. 1. The separators were wetted with the above-mentioned electrolytes when the cells were assembled. The charge/discharge characteristics of the
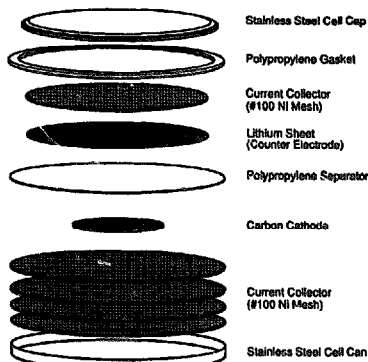
cells were evaluated by galvanostatic cycling at 0.1 mA cm^{-2} (per the area of the MCMBs anode). The cutoff voltages of the charge and the discharge were 0 and 2.0 V, respectively.

A beaker-type, three-electrode cell (50 cm^3 in electrolyte volume) was used for a.c. impedance measurements. The working electrode was identical with the above-mentioned MCMBs anode. The counter and reference electrodes were a lithium sheet (5.0 cm^2 in area) and a small lithium chip, respectively. The impedance was measured by a frequency response analyser (Solartron, 1250A) at open-circuit potential before charging of the MCMBs electrode and during charging (0.25 and 0.10 V versus Li/Li$^+$). The frequency was scanned from 65 kHz to 0.01 Hz, and the a.c. voltage was 10 mV$_{p-p}$. All electrochemical measurements were performed under a dry argon atmosphere at room temperature (20 to 25 °C).

3. Results and discussion

The voltage–time curves during the first and fifth charge/ discharge cycles of the coin-type cells with the MCMBs electrode and EC–DMC or EC–DEC containing 1 M Li(CF$_3$SO$_2$)$_2$N are shown in Fig. 2. On initial charging in both the EC–DMC and EC–DEC systems, the voltage gradually decreased to reach ~0.25 V, and then a long plateau was observed to 0 V. On the fifth charging cycle in both the electrolyte systems, the portion of the curve in the high voltage region (>0.25 V) became shorter, and the plateau remained long to 0 V. By contrast, the profiles of the discharge curve observed on the first and the fifth cycles in each system were essentially similar with a long plateau from 0 to 0.25 V and an abrupt increase to 2.0 V. In both systems, a consid-
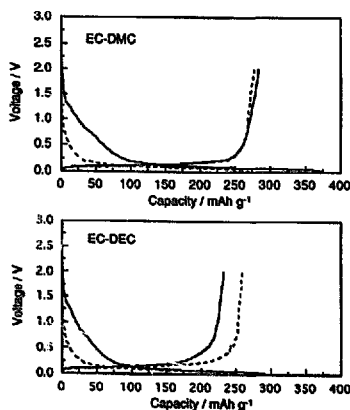

Fig. 1. Exploded view of coin-type cell hardware for charge/discharge cycling tests.

Fig. 2. (———) First and (– – –) fifth charge/discharge curves for coin-type cells with MCMBs electrode; electrolyte EC–DMC or EC–DEC with 1 M Li(CF$_3$SO$_2$)$_2$N.

erable difference was observed between the first charge capacity and the first discharge capacity. This 'retention' disappeared after the first cycle in both the electrolyte systems. The retention at the first cycle, as well as the above-mentioned profiles of the charging and discharging curves, is typical of highly graphitized electrodes for rechargeable lithium batteries [8–12]. The retention ascribed to the decomposition of electrolyte components on the charge process and/or lithium remaining in the host carbon on the discharge process is known to be inevitable in most systems [8–12]. If the retention does not induce degradation of charge/discharge capacity and cycleability, it will do no harm [13]. It often happens that the film that results from the decomposition of the electrolyte on the surface of the electrode during charging covers and inactivates the active sites of the carbon inducing undesirable side reactions [13].

The cycle dependence of the discharge capacity of the MCMBs electrode was observed using the coin-type cells with EC–DMC or EC–DEC electrolytes, as shown in Fig. 3. For the EC–DMC electrolyte system, the discharge capacity is almost stable during cycling, while the discharge capacity in the EC–DEC system gradually increases until about the sixth cycle to reach the same capacity as the EC–DMC system (270 to 280 mAh g^{-1}). It has been reported [10] that the maximum discharge capacity of MCMBs graphitized at 2800 °C is ~282 mAh g^{-1}, taking into account the existence of a turbostratic structure between the graphite layers of the graphitized MCMBs. Therefore, $Li(CF_3SO_2)_2N$ is regarded as one of most attractive electrolytic salts for highly graphitized carbon electrodes (such as MCMBs graphitized at 2800 °C) because it guarantees a stable discharge capacity nearly equal to 'maximum capacity', even at repeated cycling. Except for the first cycle, the coulombic efficiency of each
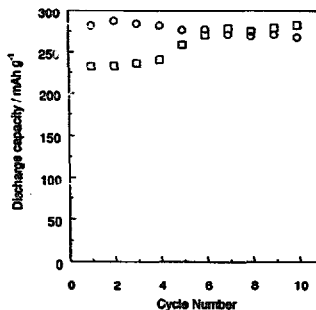

Fig. 3. Cycle dependence of discharge capacity of coin-type cells with MCMBs electrode; electrolytes: (O) EC–DMC and (□) EC–DEC with 1 M $Li(CF_3SO_2)_2N$.

charge/discharge cycle is estimated to be almost 100% in both the electrolyte systems.

In order to determine the interfacial characteristics between the MCMBs electrode and the electrolytes during charging, a.c. impedance measurements of the electrode were carried out. Cole–Cole plots observed before and during charging the MCMBs electrode at each potential in the EC–DMC and EC–DEC systems are given in Fig. 4. The arc that appears in the high frequency region (corresponding to the left part of each profile) should be due to the charge-transfer process between lithium ions and the host carbon and not to the film derived from the decomposition of electrolytes at the interface during charging. This is because the arc is observed even before charging. No change in the shape of the arc in the high-frequency region was observed in each electrolyte system during charging. The arc observed in the EC–DEC
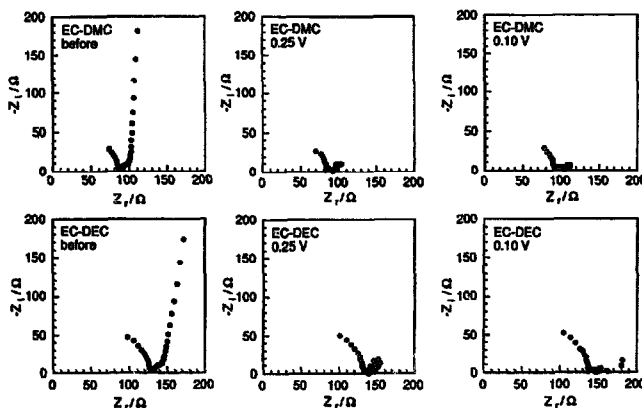

Fig. 4. Cole–Cole plots before and during charging MCMBs electrode at each potential (0.25 and 0.10 V vs. Li/Li$^+$) in EC–DMC and EC–DEC electrolytes with 1 M $Li(CF_3SO_2)_2N$.

system was somewhat larger than that in the EC–DMC system. This suggests that the interfacial resistance in the EC–DEC system is larger than that in the EC–DMC system. The difference of resistance between the two systems on initial charging correlates with the difference between the first discharge capacities of the corresponding systems, as shown in Figs. 2 and 3. It is notable that the appearance of a new arc, as well as an increase in the size of the original arc due to the film formation, in the Cole–Cole plots can be barely observed during charging to negative potentials. On the other hand, the film formation that is obviously detectable by the a.c. impedance analysis (in this case, therefore, the film has high resistance) on first charging has been reported in most electrolyte systems containing $LiPF_6$. Usually, the film formation has been observed below ~ 1 V during first charging of the surface of the highly graphitized carbon electrodes [11–13]. Even if the film was formed during the first charging process in the electrolyte containing $Li(CF_3SO_2)_2N$, the film resistance would be low, as suggested by the a.c. impedance response observed in Fig. 4. Thus, in $Li(CF_3SO_2)_2N$ systems, the retention shown in Fig. 2 should not contribute to the film formation inducing the degradation of the discharge capacity.

In conclusion, $Li(CF_3SO_2)_2N$ — lithium imide — provides a stable interface between an MCMBs electrode and various electrolytes during charging. This desirable property suggests that the MCMBs electrode will display stable and excellent charge/discharge performance in EC-based electrolytes containing $Li(CF_3SO_2)_2N$.

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