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How does lithium oxalyldifluoroborate enable the compatibility of ionic liquids and carbon-based capacitors?

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HIGHLIGHTS

- We report a new kind of electrolyte system based on LiODFB and acylamino groups.
- Various molar ratios of electrolyte systems were thoroughly investigated.
- The novel electrolytes show excellent compatibility with carbon-based capacitors.
- The specific capacitance of EDLC reaches up to 154.2 F/g at 20 mA g^{-1}.

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ABSTRACT

Lithium oxalyldifluoroborate (LiODFB) has several unique characteristics, such as high ionic conductivity over a wide temperature range and the ability to form and stabilize solid electrolyte interface films on graphite surfaces. A series of binary, room-temperature, molten electrolytes composed of LiODFB and organic compounds with acylamino groups (acetamide, oxazolidinone or OZO) have been synthesized. Fourier-transform infrared (FT-IR) spectroscopy indicates that C=O and N–H functional groups undergo blue or red shifts upon addition of LiODFB. The electrolytes have excellent thermal stabilities and electrochemical characteristics that allow them to be promising electrolytes for electrochemical double layer capacitors (EDLCs). Here, we examine 1:5 molar ratio LiODFB and acetamide/OZO ionic liquid (IL) electrolytes in EDLCs. IL compatibility with two types of carbon-based electrodes is investigated theoretically and experimentally. We simulate possible structures and ion diameters for the ILs, which must be compatible with pore sizes of the carbon electrodes. Mesoporous activated carbon AC2, with a pore size similar to the ionic diameter of LiODFB–acetamide, has a specific capacitance of 154.2 Fg^{-1} at 20 m Ag^{-1}. Additionally, typical capacitive and reversibility behaviors can be seen in the charge–discharge curves over 0–2 V. Finally, the EDLCs exhibit good charging/discharging performances.

1. Introduction

As potential energy storage devices, electrochemical double-layer capacitors (EDLCs) are promising candidates because they have high power density and prolonged life cycles. Carbon-based EDLCs are key energy storage systems for hybrid electric vehicles [1–5]. Research on EDLCs has been focused on increasing energy density without deteriorating power density and cycle life. Because the electrical energy stored in EDLCs is a function of charge separation in the double layer across the electrode/electrolyte interface,

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the performance of EDLCs depends strongly on both the electrolyte and the porous carbon electrodes [6].

Porous carbon electrodes with high surface areas and porosities compatible with the ionic sizes in the electrolyte are crucial factors for high double-layer capacitance in EDLCs. Largeot et al. [7] investigated the relationship between ions and pores in EDLCs, and demonstrated that pores having the maximum capacitance have similar dimensions to that of the ions. In terms of rate capability to facilitate ion transfer, the pore size should be several times larger than the ions. Therefore, a good match between the pore size of the carbon material and the dimensions of the ionic species is vital to achieve advanced EDLCs with high capacitances and good rate capabilities.

High-performance EDLC electrolytes have excellent conductivity, wide operating temperature ranges, large voltage windows, adequate stability during charge–discharge cycles, and low viscosities. Recently, room-temperature molten salts, or ionic liquids (ILs), which are composed entirely of ions [8–10], have been extensively studied because of their superior electrolytic properties for high-energy-density applications [11]. These attributes include a wide liquid phase range, high thermal and electrochemical stability, very low vapor pressure, and high ionic conductivity [12]. Additionally, ionic liquids are considered safer than conventional organic electrolytes because they are less flammable and less reactive [12–14]. Most IL systems contain organic, alkyl-substituted, nitrogen-containing cations combined with a variety of anions. Because of synthetic difficulties and the high cost of many cation precursors, affordable and easily prepared IL systems are a challenge.

Several complex systems formed from amide and alkali-metal nitrates or ammonium nitrates have been studied as ion or proton-transfer materials [15,16]. ILs with acyl amino groups can coordinate with Li^+ cations, which can weaken the reciprocity between corresponding bonds and thus dissociate cations and anions. Acetamide and 2-oxazolidinone (OZO) are potential candidates that have high dielectric constants ($\varepsilon = 41, 18.2$ for acetamide and OZO, respectively), and low vapor pressure. In our previous study, we demonstrated that lithium oxalyldifluoroborate (LiODFB)-based organic electrolytes exhibited preferable properties relative to those of $LiBF_6$. Those properties include high ionic conductivity over a broaden temperature range, high-temperature operation, the ability to support high-capacity lithium ion batteries that deliver at low temperature and high current rates, and safety protection against abuse [17–22]. In addition, lithium bis(oxalate) borate participates in the formation and stabilization of solid electrolyte interface films on graphite surfaces [23].

Here we discuss the facile preparation of novel binary electrolytes based on LiODFB and the ionic liquids acetamide and 2-oxazolidinone (OZO), which aim to be applied in EDLCs. The thermal and physicochemical properties of the electrolytes are characterized as a function of the LiODFB–acetamide/OZO molar ratio (1:3–1:7). It was found that the optimum molar ratio was 1:5. Calculations of the electrolyte ion sizes (diameters) were also performed. Finally, galvanostatic charge/discharge and rate capability tests were carried out to examine the compatibility between the electrolytes and two different carbon electrode materials.

2. Experimental

2.1. Preparation of electrolyte systems

LiODFB (Hongyang Chemical, China,>99.9%) was dried at 140 °C for 12 h in vacuum. Acetamide (Acros Inc., AP) and OZO (Acros Inc., 99%) were dried at 55 °C for 12 h in vacuum. Water content of the dried samples was analyzed with a Karl Fisher titrate and indicated $\leq$30 ppm. All electrolyte systems were prepared by mixing LiODFB and the organic compounds at various molar ratios (LiODFB:OZO/acetamide = 1:3–1:7) in an argon-filled ($H_2O < 5$ ppm) glovebox MBraun LabMaster 130.

2.2. Ionic conductivity and spectroscopy measurements

Ionic conductivity of the electrolytes was measured with a Pt electrode in an electrochemical cell over the temperature range −40 °C to 90 °C. The cell constant was determined with a standard KCl solution (0.01 M) at 25 °C. Alternating current impedances of the samples were measured with a CHI604D electrochemical workstation (China).

Melting point of the binary electrolytes were measured with a TA Instruments MDSC 2910 differential scanning calorimetry (DSC) by sealing 10 mg of the sample in an aluminum pan. The pan and sample were initially cooled to −100 °C with liquid nitrogen and then heated to 100 °C at a rate of 5 °C/min. The thermal stability measurements were performed under a N_2 atmosphere with a thermo-gravimetric analyzer Netzsch TG209 F1 (Germany) from ambient temperature to 550 °C at a scan rate of 10 °C/min.

Attenuated total reflection Fourier transform-infrared (ATR-FTIR) spectra of the samples were recorded on a NICOLET6700 FT-IR spectrometer (USA) over the range 4000–400 cm^{-1} with 2 cm^{-1} resolution.

2.3. Properties of carbon materials

Two types of carbon materials (AC1 and AC2) were used as electrodes for the ELDCs. N_2 (77 K) adsorption/desorption isotherms of the carbons were measured with a Quantachrome NOVA 1200 (USA) sorption analyzer. The specific surface area and pore size distribution were obtained using BET (Brunauer–Emmett–-Teller) and DFT (density functional theory) methods, respectively.

2.4. Preparation of EDLC

The electrodes were prepared by mixing 80 wt.% carbon materials, 10 wt.% acetylene black, and 10 wt.% polyvinylidene fluoride binder dissolved in NMP (1-methyl-2-pyrrolidinone)solvents. The mixed slurry was coated on a aluminium foil and the coated electrodes were dried at 120 °C for 12 h in vacuum. Coin-shaped EDLCs were assembled with the two carbon electrodes separated by a polypropylene membrane. All were immersed in the binary electrolytes and sealed in a test cell in the argon-filled glovebox (Fig. 1). Galvanostatic cycling was conducted between 0-2 V at a current density of 20 m Ag^{-1}.

3. Results and conclusions

3.1. ATR-FTIR analysis

The vibrational spectrum of acetamide has been extensively studied [24]. Fig. 2 displays FT-IR spectra for N–H and C=O stretching vibrations in acetamide and in different molar ratios of LiODFB–acetamide. Previous studies [25] have suggested that acetamide works as a complexing agent for both the cations and anions because of its two polar groups (C=O and NH_2). On the basis of considerations discussed above, acetamide is a favorable solvent for electrolytes because it is nucleophilic and electrophilic, and it has a large dipole moment and a high dielectric permittivity. Acetamide itself can form hydrogen bonds via the O in the C=O groups and the H in the N–H groups, resulting in asymmetric and symmetric stretching vibrations at 3290 cm^{-1} and 3149 cm^{-1}, respectively. When the lithium salt LiODFB is added, Li^+ can