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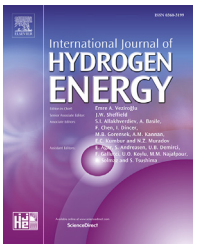

Influence of acrylic acid on ethylene carbonate/dimethyl carbonate based liquid electrolyte and its supercapacitor application

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ABSTRACT

A liquid electrolyte based on binary solvent systems of ethylene carbonate (EC), dimethyl carbonate (DMC) and lithium bis(trifluoromethane)sulfonimide (LiTFSI) salt incorporating with acrylic acid (AA) monomer was synthesized. The ionic conductivity studies revealed that the conductivity of the liquid electrolyte was enhanced from 2.16×10^{-3} to 2.24×10^{-3} S cm^{-1} at room temperature after the addition of 0.1 mol/kg AA due to the presence of a carbonyl group in AA structure. The viscosity and the temperature dependence of the ionic conductivity followed an Arrhenius equation. Interactions of the EC/DMC, LiTFSI and AA were characterized by Fourier transform infrared spectroscopy analysis. The electrochemical performance of the liquid electrolyte towards electric double layer capacitor (EDLC) was investigated using cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy techniques. EDLC performances demonstrated that the supercapacitors exhibited specific capacitance ~24.01 F/g at 5 mV/s. The life cycle test revealed that supercapacitor cell incorporated with synthesized liquid electrolyte possessed excellent stability and coulombic efficiency even after 4000 cycles.

Introduction

Electrochemical capacitors or supercapacitors (SCs) are one of the energy storage devices which can bridge the gap between the batteries and conventional capacitors. Owing to their ability to store high energy density, fast charging and long cycling durability, SCs are considered as a potential replacement for batteries in industrial application [1,2]. On the basis of the charge storage mechanism, supercapacitors can be classified into two categories; electrical double layer capacitors (EDLCs) and pseudocapacitors. In EDLC, energy is stored in the double layer at interface between electrode and electrolyte without faradaic process, while for pseudocapacitor, energy is stored through Faradaic redox process [3,4].

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Numerous works have been done in producing ion-conducting materials for improving the performance of electrochemical devices. Liquid electrolytes that consist of mixed alkyl carbonates that can dissolve lithium salts have catalysed progress in various electrochemical devices [5,6]. In efforts to develop an improved performance of liquid electrolyte, membrane additives are introduced to the electrolyte systems in order to produce higher ionic conductivity in a wide temperature range of operation [7,8]. In the present study, acrylic acid (AA) monomer has been chosen as the additive in the binary solvent system of ethylene carbonate (EC) and dimethyl carbonate (DMC) with lithium bis(trifluoromethane) sulfonimide (LiTFSI) as the lithium salt. AA is the simplest unsaturated carboxylic acid which has double bond and carboxyl group in C_3 one molecule with the formula $CH_2{=}CHCOOH$. The vinyl group is attached to the carbonyl carbon directly. Although AA monomer appears as one of the most fundamental system to be studied, it is difficult to avoid its polymerization under current experimental conditions. Furthermore, the effect of addition of monomer on structure and spectroscopic behaviour of the liquid electrolyte complex is still limited [9–13].

Herein, the effect of the addition of different concentrations of AA on structural, rheological and electrical properties of liquid electrolyte system of EC/DMC: LiTFSI is evaluated. In addition, the electrochemical performance of the liquid electrolyte system towards EDLC is also investigated via cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) techniques.

Experimental

Materials

Ethylene carbonate (EC) (98% purity, Aldrich), dimethyl carbonate (DMC) (Reagent Plus 99%, Sigma–Aldrich), lithium bis(trifluoromethane)sulfonimide (LiTFSI) (97% purity, Sigma–Aldrich), acrylic acid (AA) monomer (contains ≤ 180–200 ppm MEHQ as inhibitor, 99%, Aldrich), poly(vinylidene fluoride) (PVdF) binder (from Aldrich) and 1-methyl-2-pyrrolidone (NMP) (≥99% Sigma-Aldrich), activated carbon (AC) (Kuraray Chemical Co. Ltd., Japan) and Carbon black (Super P) were used as received.

Preparation of liquid electrolyte

In the typical synthesis of electrolyte, first EC and DMC were mixed (1:1 wt%) with total mixture of 15 mL, followed by the addition of 0.058 mol/kg LiTFSI salt. After this, 0.1 mol/kg of AA monomer was subsequently added into the above mixture. The final mixture was stirred for 8 h at room temperature until transparent homogenous mixture was obtained. Similar steps were repeated with different concentrations of AA as tabulated in Table 1.

Table 1 – Designations of the developed liquid electrolytes with its respective AA concentrations.

Sample designation	Concentration of AA (mol/kg)
AA 0	0
AA 0.1	0.1
AA 0.2	0.2
AA 0.3	0.3
AA 0.4	0.4
AA 0.5	0.5
AA 0.6	0.6
AA 0.7	0.7
AA 0.8	0.8
AA 0.9	0.9
AA 1.0	1.0

Characterization of liquid electrolyte

The ionic conductivity of the liquid electrolytes was evaluated by AC impedance spectroscopy using a LCR Hi-Tester (Model: Hioki - 3532-50, Japan) over the frequency range from 42 Hz to 5 MHz at a signal level of 10 mV. The conductivity values (σ) can be calculated from the bulk resistance (R_b), which is determined by the following equation:

$$\sigma = \frac{L}{R_b A} \quad (1)$$

where L is the sample holder length (cm), A is the surface area of electrode (cm^2), and R_b is the bulk resistance of the electrolyte. Viscosity studies were carried out within the temperature range of 25–100 °C using LAUDA iVisc Viscometer with Visco-cool 6 thermostat to maintain temperature of liquid electrolytes. FTIR spectra were recorded with Thermo Scientific Nicolet iS10 spectrophotometer, which was in the region from 500 to 2000 cm^{-1} at a resolution of 1 cm^{-1}.

Fabrication of electrode

The electrode was fabricated by mixing 75 wt% AC, 15 wt% carbon black and 10 wt% PVdF in NMP solvent until homogeneous slurry was obtained. The slurry was then coated on 1 cm^2 diameter stainless steel foil and dried in an oven at 100 °C for 12 h. The average mass loading of the active material was found to be 1.3 ± 0.1 mg.

Fabrication of symmetric supercapacitor

The supercapacitor was fabricated by the configuration of AC/liquid electrolyte complex with filter paper as separator/AC. The supercapacitor was placed in a cell kit for further electrochemical analyses.

Supercapacitor characterization

All supercapacitor studies were performed using Gamry Potentiostat/Galvanostat/ZRA (Model: Interface 1000, USA). In order to investigate the performance symmetric supercapacitor, CV was performed in a potential window ranging from −1 to 1 V at different scan rates (5–500 mV/s). The GCD curves were obtained at different current densities (25–600 mA/g) in a potential window from 0 to 2 V. The EIS was perform in a frequency range from 0.01 Hz to 100 kHz. The coulombic efficiency (α) was calculated by the following formula: