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Cesium carborane as an unconventional non-aqueous electrolyte salt for electrochemical capacitors

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ABSTRACT

A novel electrolyte salt for non-aqueous electrochemical capacitors, cesium carborane, was electrochemically characterized in two organic solvent systems at different concentrations–acetonitrile and a 1:1 mixture of ethylene carbonate and dimethyl carbonate. It was found that Cs^+ ion specific adsorption takes place, being dependent on the electrolyte concentration and on the solvent used. Stronger specific adsorption effect with partial charge transfer was observed from the acetonitrile based electrolytes, where the cesium salt has low solubility.

1. Introduction

The enhancement in the power and energy performance of the electrochemical capacitors is mainly focused on developing new electrode materials of high capacitance, such as carbon nanostructures of different surface chemistry and texture, redox active metal oxide or electrically conductive polymer based materials, intercalation compounds, electrochemical hydrogen storage materials, etc. [1,2]. However, the chemical composition and surface morphology (i.e., wetting properties) of separators [3] as well as the properties of electrolytes, e.g., improved ion adsorption characteristics, electrochemical stability and compatibility with electrode materials, are equally important features that have to be addressed in the development of high performance electrochemical capacitors of extended life time. The conventional non-aqueous electrochemical capacitor electrolytes, e.g., alkyl ammonium salts in acetonitrile (AN) or in propylene carbonate (PC), allow applying cell potentials up to 2.7 V while maintaining long-lasting cyclability. It is important to find alternatives of improved electrochemical stability that allow applying higher cell potentials and, if possible, to increase the capacitance of the electrode/electrolyte interface by reversible faradaic reactions or specific adsorption of the electrolyte ions.

Specific adsorption of halide ions on the bismuth single crystal planes has been demonstrated with the strongest effect established for the I^- ions in aqueous and non-aqueous electrolytes [4,5]. The redox-active I^-based aqueous electrolytes [6–8] as well as I^-containing ionic liquid mixtures [9,10] and redox-active Br^-ionic liquids [11], have been thoroughly studied for carbon based electrochemical capacitor applications. Weak specific adsorption effect was also observed for ClO_4^-anions in aqueous electrolyte [12]. The influence of the specific adsorption of bulky tetraalkylammonium cations on the charge-compensation mechanism in carbon micropores, together with the effect of coupling confined specific adsorption of cations and charge-induced desorption of anions, has been analyzed in Ref. [13]. Ion solvation and distortions in the solvation shell (partial removal) during the adsorption process at micro-meso-porous carbon electrodes depend on the combination of solvents and ions, and thus have direct effect on the capacitance of the electrode/electrolyte interface [14].

In this study novel non-aqueous electrolytes based on a superacid salt cesium carborane ($CsCB_{11}H_{12}$) are tested in order to describe the specific adsorption effects in relation to the electrolyte solvent used and to establish the electrochemical behavior of a large spherical carborane anion. For better comparison, electrolytes of different concentration were prepared in the traditional electrochemical capacitor solvent AN, and in an environmentally friendlier solvent system of ethylene carbonate (EC) and dimethyl carbonate (DMC), commonly applied in Li-ion batteries [15], but also tested for carbon based electrical double layer and hybrid electrochemical capacitors with Li- and Na-salt electrolytes [16–20].

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2. Experimental

Two- and three-electrode special hermetic aluminium test cells ('2TC' and '3TC', Hohsen Corp.) were assembled for the electrochemical characterization by cyclic voltammetry and electrochemical impedance spectroscopy methods (1252A Solartron frequency response analyzer and SI1287 potentiostat with a 5 mV modulation).

Carbide derived carbon powder was synthesized from molybdenum carbide by the high-temperature chlorination method at 800 °C, noted as $C(Mo_2C)$, and was mixed with polytetrafluoroethylene (60% solution in H_2O (Aldrich)) to form a paste with 5 wt% binder content. Thin ($\sim 105 \pm 5$ μm) electrode layers were roll-pressed from the active material paste and ~2 μm thick Al layer was deposited onto one side of the electrode layer by the magnetron sputtering method (AJA International) to reduce the ohmic potential drop (*IR*-drop). The $C(Mo_2C)$ powder specific surface area was $S_{BET} \approx 1675\,m^2\,g^{-1}$, calculated from the Brunauer-Emmett-Teller theory, and micropore area from the *t*-plot method was $S_m \approx 1560\,m^2\,g^{-1}$ with two main pore size distribution maxima located at 1.15 nm and 3.80 nm. After preparing the electrode layers from powder and the Al-deposition, less than 10% decrease was measured for both total specific surface area and microporous surface area ($1535\,m^2\,g^{-1}$ and $1480\,m^2\,g^{-1}$, respectively). More precise physical characterization (Raman and XRD analysis) of the partly graphitized amorphous $C(Mo_2C)$ powder can be found in Ref. [21].

The electrochemically tested $CsCB_{11}H_{12}$ (Strem Chemicals) electrolytes were 0.1 M and 0.2 M solutions (saturation concentration ~0.22 M) in AN (99.9%, max 0.003% H_2O, Riedel-de Haën), and 0.3 M, 0.5 M and 0.8 M solutions (saturation concentration >0.8 M) in an equimolecular mixture of EC (Selectipur®, Merck) and DMC (> 99%, H_2O < 0.002%, Sigma-Aldrich). All test cells were assembled in a glove box (O_2 and H_2O < 0.1 ppm, MBraun). The specific ionic conductivities (κ) of the electrolyte solutions were measured using a self-prepared conductivity cell with platinum plate electrodes, for which the cell constant was determined from the measured values of the high-frequency impedance for two standard electrolyte solutions of known ionic conductivities: 0.1 M and 0.01 M KCl aqueous solutions at T = 23 °C.

The cross-sectional surface area of the working electrodes (WE) and counter electrodes (CE) in 3TCs was 0.28 cm^2 and 2.0 cm^2, respectively, and 2.0 cm^2 for both electrodes in 2TCs. The carbon loading of electrodes was $\sim 5.5\,mg\,cm^{-2}$. The reference electrode (RE) was Ag/AgCl in the same electrolyte solution (+0.2 V vs. SHE), prepared by depositing a layer of AgCl on a positively polarized Ag wire from 0.1 M HCl aqueous solution. Mesoporous polypropylene separator (Celgard® 2400) was applied in the systems with carbonate solvent mixture based electrolytes, and cellulose separator (TF4425, Nippon Kodoshi) with the acetonitrile based electrolytes for better chemical compatibility [16,17,21,22].

A simple notation system was adapted for the test systems, e.g., 0.2AN-2TC indicating a two-electrode test cell based on 0.2 M $CsCB_{11}H_{12}$ solution in acetonitrile. All the calculation methods used have been explained in a previous publication [16].

3. Results and discussion

3.1. Electrolyte ionic conductivities

The measured electrolyte κ values are presented in Table 1, together with some electrolytes studied earlier [16–19]. Despite the low concentration, the κ value for 0.1 M $CsCB_{11}H_{12}$ electrolyte in a low-viscosity AN solvent (10.6 mS cm^{-1}) is comparable to the 1 M solutions of Li- and Na-salt electrolytes with symmetric $PF_6{}^-$ and $ClO_4{}^-$ anions in a more viscous EC:DMC mixture, and higher κ was measured for 0.2 M $CsCB_{11}H_{12}$ + AN. The measured κ value of 8.9 mS cm^{-1} for 0.5 M $CsCB_{11}H_{12}$ solution in EC:DMC is rather close to the values for 1 M solutions of $NaClO_4$ and $NaPF_6$ in the same solvent mixture ($\kappa \approx 9.15$ mS cm^{-1}), indicating that the larger Cs^+ and $CB_{11}H_{12}{}^-$ ions are not strongly solvated in the mixture of carbonates (also in AN). The $CB_{11}H_{12}{}^-$ anion has the lowest nucleophilic ability even known [23], and has an estimated diameter of 1.04 nm, which is slightly smaller than the first pore size distribution maximum for the $C(Mo_2C)$ carbon, located at 1.15 nm [24].

3.2. Cyclic voltammetry measurements for three-electrode test cells

Cyclic voltammograms (CVs) were measured in various working electrode potential regions at potential scan rates (ν) from 0.5 to 50 mV s^{-1}. Nearly rectangular shape of CVs can be observed for all the systems under study in a working electrode potential (E) region from -2.0 to 1.0 V (vs. Ag/AgCl), characteristic to the nearly ideal capacitive behavior with working electrode capacitance C_{WE} (Figs. 1 and 2). CVs measured at 1 mV s^{-1} for 0.2AN-3TC (Fig. 1a) show a large capacitive peak at the negative potential scan direction (cathodic scan) at $E \sim$ -2.2 V. Quick capacitance increase at more negative potentials (E < -2.35 V) is probably initiated by the faradaic reduction of the electrolyte and/or reduction of the water/oxygen traces in the electrolyte. Taking into account the well expressed concentration dependence of C_{WE}, the peak at $E \sim$ -2.2 V could be attributed to the Cs^+ cation specific adsorption on the micro-meso-porous carbon surface with partial charge transfer, as the peak capacitance is nearly two times lower in a more dilute 0.1 M $CsCB_{11}H_{12}$ + AN electrolyte system (Fig. 1b).

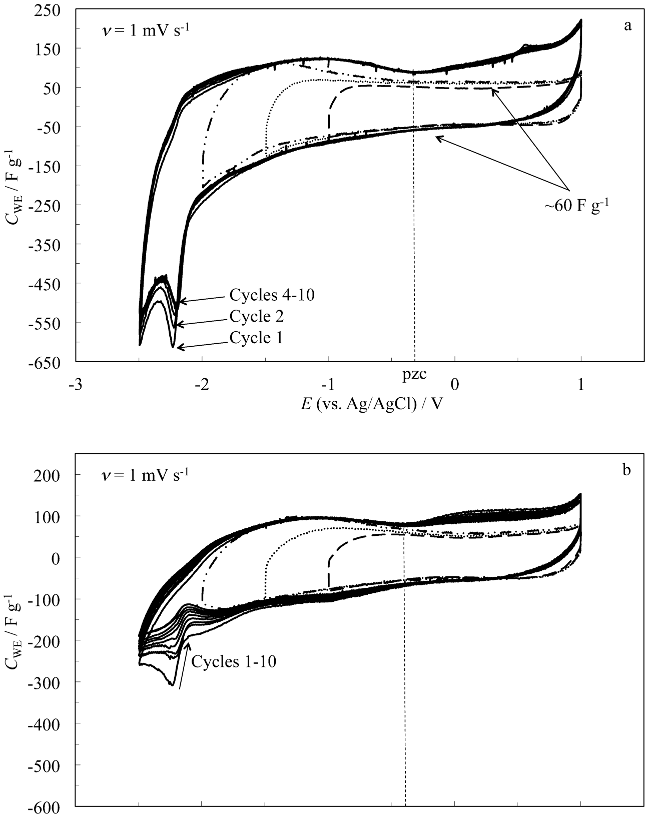

Fig. 1. Cyclic voltammograms expressed as working electrode gravimetric capacitance C_{WE} vs. potential E for 3TCs with 0.2 M (a) and 0.1 M (b) $CsCB_{11}H_{12}$ electrolytes in AN.