



NaClO₄ and NaPF₆ as potential non-aqueous electrolyte salts for electrical double layer capacitor application

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ABSTRACT

1 M NaClO₄ and 1 M NaPF₆ electrolyte solutions in ethylene carbonate–dimethyl carbonate solvent mixture (1:1 by volume) were studied for the possible application in electrical double layer capacitors (EDLCs) with carbide-derived carbon electrodes (synthesized from Mo₂C). Two- and three-electrode test cells were electrochemically characterized by using cyclic voltammetry, constant current charge/discharge and electrochemical impedance spectroscopy methods. Region of ideal polarizability, values of series capacitance, high-frequency resistance, time constants, etc. have been established. Based on the specific energy and power calculations, and other characteristics, it was found that the Na-salts based EDLC test cells have similar electrochemical behavior compared to LiPF₆ and LiClO₄ based systems that have been studied earlier. The studied Na-salts based electrolytes are potential candidates for EDLCs, however, future improvement of the cyclability is inevitable to achieve long-lasting high performance.

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1. Introduction

Electrical double layer capacitors (EDLCs) [1–10] and lithium ion batteries [11–14] are energy storage devices with high power and energy capabilities, respectively, being under continuous development for different applications needing high-quality electric power supply. The use of electrochemical energy conversion/storage devices is essential to gradually become free of the dependence on the fossil fuels for electric energy production, and has a substantial effect on the environment. Different Li-salts in non-aqueous solvents have been studied and applied as electrolytes for Li-ion batteries with high energy content and good efficiency. A few Li-salts have also been tested for EDLC systems by the authors of this paper, published in Refs. [15,16]. Unfortunately, the world lithium resources are very limited and thus, the development of energy storage devices is moving in the direction of materials and chemical compounds based on the elements that are abundant – C, Si, Na, etc. Consequently, sodium salts, based on the same anions as the Li-salts studied earlier [15,16], were tested as EDLC electrolyte salts in this paper to analyze if Na-salts can be used as electrolytes in high energy/power density EDLCs. In a recent paper by Komaba et al. [17] Na⁺ ion containing electrolytes have been tested to develop a Na-ion battery composed of hard disordered carbon anode and a layered-type cathode, analyzing the solid electrolyte

interface formation kinetics and properties as well as the influence of solid electrolyte interface on the hard disordered carbon anode cyclability.

2. Experimental

A high surface area carbide-derived carbon powder, used as electrode active material (hereafter noted as C(Mo₂C)), was synthesized from molybdenum carbide by the high-temperature chlorination method at 800 °C, described in detail in [18]. The ~105 ± 5 μm thick electrodes were press-rolled from slurries comprising of 95 wt% C(Mo₂C) powder and 5 wt% polytetrafluoroethylene (PTFE) binder (60% solution in H₂O (Aldrich)). A ~2 μm thick Al layer was deposited onto one side of the electrodes by magnetron sputtering method (AJA International) for good electrical contact and to reduce the ohmic potential drop (*IR*-drop) during charge/discharge process. The X-ray diffraction (XRD), Raman spectroscopy and nitrogen adsorption data for the C(Mo₂C) powder were analyzed in Ref. [18]. The specific surface area of C(Mo₂C) powder was 1680 m² g⁻¹ (Brunauer–Emmett–Teller method), micropore area and micropore volume were, respectively, 1560 m² g⁻¹ and 1.2 cm³ g⁻¹ (*t*-plot method), and total pore volume was 1.4 cm³ g⁻¹. Thus, C(Mo₂C) applied was mainly microporous with some mesoporosity. Based on XRD and Raman data, C(Mo₂C) was mainly amorphous [18], without remarkable graphitic areas in the electrode material.

The electrolytes studied were 1 M solutions of NaClO₄ (ACS reagent, ≥ 98%, Sigma–Aldrich) or NaPF₆ (98%, Aldrich) in equimolecular mixture of ethylene carbonate (EC) and

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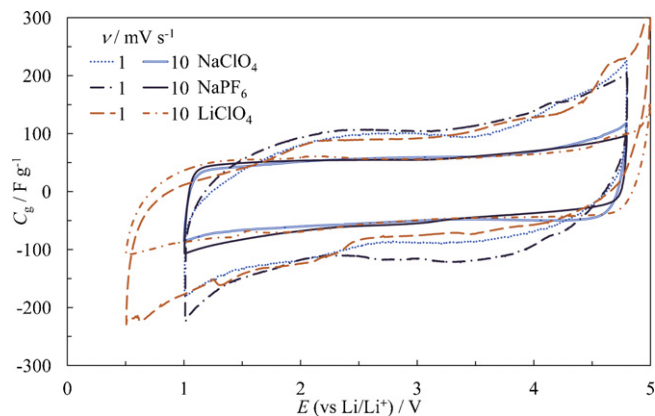


Fig. 1. CVs for NaClO₄, NaPF₆ and LiClO₄ based three-electrode test cells, presented as gravimetric capacitance vs. WE potential (vs. Li/Li⁺ RE) at different potential scan rates ν .

dimethylcarbonate (DMC) (Merck, Selectipur®). The solutions were saturated with pure Ar (99.9999%) and all measurements were conducted in a glove box using hermetic two- and three-electrode standard test cells (Hohsen Corp.). Working electrodes (WE) and counter electrodes (CE) in three-electrode systems had cross-section surface areas of 0.28 cm² and 2.0 cm², respectively. Reference electrode (RE) was Li-ring (Li/Li⁺) in the same electrolyte solution (negligible amount of Li-salts was added to the electrolytes for the establishment of potential). Cross-section surface area was 2.0 cm² for both electrodes in two-electrode measurement systems for life-time tests. Mesoporous polypropylene (Celgard® 2400) membrane was used as separator between C(Mo₂C) electrodes, impregnated with the working electrolyte solution for 24 h before measurements. Impedance spectra were recorded using a 1252 A Solartron frequency response analyzer and a SI1287 potentiostat with a 5 mV modulation.

The EDLC test cells (TC) based on 1 M NaClO₄ + EC + DMC and 1 M NaPF₆ + EC + DMC electrolytes are hereafter noted as NaClO₄-TC and NaPF₆-TC, respectively.

3. Results and discussion

3.1. Cyclic voltammetry measurements for three-electrode test cells

The cyclic voltammograms (CVs) were measured for the three-electrode test cells at potential scan rates ν from 0.5 mV s⁻¹ to 50 mV s⁻¹ to establish the region of ideal polarizability of the C(Mo₂C) electrodes in the Na-salts based non-aqueous electrolytes. According to the CVs given in Fig. 1, measured at $\nu = 1$ and 10 mV s⁻¹ and presented as gravimetric capacitance C_g (F g⁻¹) vs. WE potential E (vs. Li/Li⁺), the negative and positive electrode potential limits for the Na-salts based TCs are $E > 1.0$ V and $E < 4.8$ V, respectively. At E outside this potential region faradaic processes start to take place extensively, such as decomposition of the electrolyte solvent or salt, reduction of trace O₂ and H₂O and oxidation/reduction of electrode surface functionalities. CVs for LiClO₄ + EC + DMC based TC [16] were added for comparison in Fig. 1. The LiClO₄ based TC allowed applying electrode potentials ~0.5 V more negative without a noticeable increase in current densities, different from Na-salts based TCs, where the current density increase was remarkable at $E < 1.0$ V (not shown in the figure). This might be due to the differences in Li⁺ and Na⁺ solvation energies and also related to the solid electrolyte interface formation kinetics at electrode surface at $E < 1.0$ V (vs. Li/Li⁺) [16]. However, inside the region of ideal polarizability, the C_g values for the three systems compared are rather

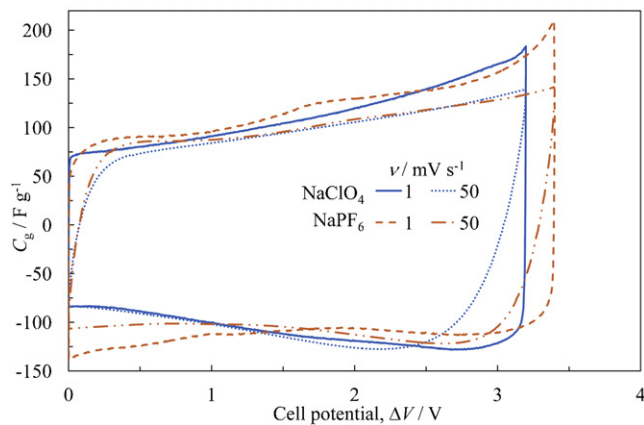


Fig. 2. CVs for two-electrode NaClO₄-TC and NaPF₆-TC, presented as gravimetric capacitance vs. cell potential at different potential scan rates ν .

similar. According to the CVs at $\nu = 1$ mV s⁻¹, slightly higher capacitance values have been calculated for the NaPF₆-TC compared to other salts, and at $\nu = 10$ mV s⁻¹ C_g is slightly higher for NaClO₄-TC at WE potentials $E > 3.5$ V.

3.2. Cyclic voltammetry measurements for two-electrode EDLC test cells

The CVs for two-electrode symmetric TCs were measured at ν from 1 to 100 mV s⁻¹. The maximal cell potentials ΔV applied were 3.2 V and 3.4 V for NaClO₄-TC and NaPF₆-TC, respectively (Fig. 2), from where forward current density started to increase strongly due to the beginning of various faradaic reactions, mentioned earlier. However, as was noticed on the basis of three-electrode measurements, the gravimetric capacitance C_g values, calculated per one working electrode according to Eq. (1), are similar for the two electrolytes studied.

$$C_g = \frac{2j \cdot S_{el}}{\nu \cdot m_{el}}, \quad (1)$$

where ν is the potential scan rate (V s⁻¹), S_{el} is the electrode cross-section surface area (2.0 cm²), m_{el} is the mass per one electrode (g), and l_{el} is the electrode thickness (105 μ m).

At $\Delta V < 1.0$ V the C_g values are slightly smaller for the NaClO₄-TC than those for NaPF₆ (or LiPF₆ [15]) electrolyte based TCs, that was also established by the impedance spectroscopy measurements (Fig. 4). The smaller C_g values could be explained by the higher solvation energy of ClO₄⁻ anions compared to PF₆⁻ anions. Therefore, the electrostatic attraction forces at $\Delta V < 1.0$ V are insufficient for the partial solvation shell removal from ClO₄⁻ anions, causing reduced anion adsorption in the porous network of C(Mo₂C) electrodes.

3.3. Impedance spectroscopy data

Nyquist plots were measured in *ac* frequency range from 1×10^{-3} to 3×10^5 Hz at different cell potentials applied (Fig. 3), where Z' is the real part and Z'' is the imaginary part of impedance [19]. The depressed semicircles at $f > 200$ Hz describe mixed kinetic processes at macroheterogeneous electrode regions [15,16,18,20] as well as the formation and electrochemical behavior of a thin passive layer on the aluminum current collectors deposited onto carbon electrodes by magnetron sputtering method. The so-called total high-frequency series resistance R_E values can be obtained from Nyquist plots at $f \rightarrow \infty$. R_E consists of electrolyte and electrode material resistances and contact resistance for Al-current collector (including thin passive layer) and porous carbon electrode interface

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