

Capacity of a glassy carbon electrode in propylene carbonate based electrolytes

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Anotation:

The capacity of glassy carbon in aprotic salt solutions in propylene carbonate (PC) is investigated as an approach to the optimisation of electrochemical supercapacitors. The strong influence of water residuum on capacities at negative potentials is indicated. The capacities exhibit a shallow minimum at potential from 0 V to +0.5 V (vss. Cd/Cd²⁺ reference electrode) and they increase with increasing electrolyte concentration. The admittance of the electrode in pure PC (as received) is by 2 – 3 orders of magnitude smaller. Undoubtedly, the properties of ions in solution influence the capacity by a factor not exceeding 2 to 5.

Kapacita skelného uhlíku v bezvodých solných roztocích v propylenkarbonátu (PC) je zkoumána z hlediska optimalizace elektrochemických superkondenzátorů. Zjištěn byl významný vliv zbytkové vody na kapacitu při negativních potenciálech. Kapacity vykazují mělké minimum při potenciálech 0 V až +0,5 V (proti Cd/Cd²⁺ referenční elektrodě) a zvyšují se s rostoucí koncentrací elektrolytu. Admitance elektrody v čistém PC je o 2 až 3 řády menší než v elektrolytech se solnými ionty. Vlastnosti iontů v roztoku ovlivňují kapacitu nejvýše 2 krát až 5 krát.

INTRODUCTION

Electrochemical supercapacitors [1] are modern components for the use as auxiliary or main power sources in many applications. Beside the capacitors based on transition metal oxides, the capacitors using double layer effects on carbon electrodes in aprotic solvents seem to be much favorable.

Main components of those capacitors are various carbonaceous electrode materials and suitable electrolytes as it is described in [1]. We try to find optimal electrolyte and we decided to make an attempt to investigate potential usage of gel polymer electrolytes, which offer several benefits known from lithium ion batteries. Therefore, we started to measure various propylene carbonate (PC) based electrolytes in contact with a glassy carbon electrode. We excluded the variability of carbon used as the electrode in this way.

Our main technique used was the impedance spectroscopy.

THEORY

Any boundary between ionic and electronic conductors is the place on which potential difference between the bulk of both phases exists. If no electrochemical reactions, *i. e.*, if no transport of mass across the boundary can proceed, then a steady potential barrier is formed from mobile ionic species. Such a boundary is called ideally polarized boundary. Then we suppose that the conductivity of electronic conductor is very high (in other words, the mobility

of charge carriers is sufficiently high), then the potential barrier is located in the ionic conductor (electrolyte). The distribution of potential in the layer directly beneath the boundary is governed by the equation

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{e_0 \rho}{\epsilon \epsilon^0} \quad (1)$$

where x is the coordinate perpendicular to the boundary. Its general solution is well known (for example, see [2]). In electrochemistry, the equations describe the properties of diffusion double layer as the influence of potential drop ψ in the double layer on the differential capacity of the space charge existing in the double layer. In general, this capacity is described by the quantity $[\Sigma \nu_i C (\psi - \psi_0)]^{-1/2}$ where the potential of zero charge is denoted as ψ_0 and the parameter $\Sigma \nu_i C$ equals to the sum of concentrations of all ions expressed as their charges.

In reality, the differential capacity of a polarized electrode is a series connection of the diffuse double layer capacity and the capacity of the layer formed by adsorption of ions and polar molecules on the interface. Further, a layer of organic or inorganic substances is usually present on the interface between an inert electrode and organic aprotic electrolyte. This layer is known as SEI or PEI interfaces and its differential impedance is more or less like to that of capacity. Finally, it is generally known that the impedance of a polarized solid electrode is not a pure capacity, but a constant phase element (C.P.E.) almost in all cases.

The investigation of the interface of glassy carbon in aprotic electrolytes seems to be important for the proper choice of the electrolyte and it must be a starting point for the study of gel polymer electrolyte in contact with carbon. This paper deals with the behavior of selected liquid electrolytes predominately, while their usage in gel polymer matrix will be described in a following paper.

METHOD AND APPARATUS

The potentiostat AUTOLAB enabled with the module FRA-2 and software GPES for cyclic voltammetry was used. A three-electrode vessel contained Pt counter electrode and Cd/Cd²⁺ pseudoreference electrode [3] based on the gel polymer electrolyte were used.

Analysis of results was done using the Boukamp software delivered with the potentiostat. An equivalence circuit containing the series resistance of the electrolyte and then a parallel combination of a quasi capacitor (exactly, a C.P.E. with phase angle from 80°C to 85°C) was suggested. The parallel resistance was considered to be a residual background current. The main part of investigations covered frequency range from 500 Hz to 0,1 Hz. The electrode was a glassy carbon rod of Ø5 mm in PTFE holder.

MATERIALS

Lithium and sodium perchlorates (0.5M to 2M), tetramethylammonium and/or lithium fluoroborate and a saturated solution of potassium perchlorate in propylene carbonate (PC) were used.

PMMA based gel polymer electrolyte was prepared from MMA monomer, the salt solution in PC and polymerization catalyst according to our previous papers [4], [5]. The salts were dried in vacuum at temperature from 100°C to 110°C before use. Propylene carbonate was used as received from Sigma-Aldrich.

RESULTS

An example of a cyclic voltammogram in PC – LiClO₄ electrolyte is depicted in Fig. 1. We can see the behavior similar to a capacitor at potentials more positive than -0.4V or more. A small peak appears between -0.6 V and -0.4 V, which may correspond to the formation of the SEI layer by reduction of the electrolyte.

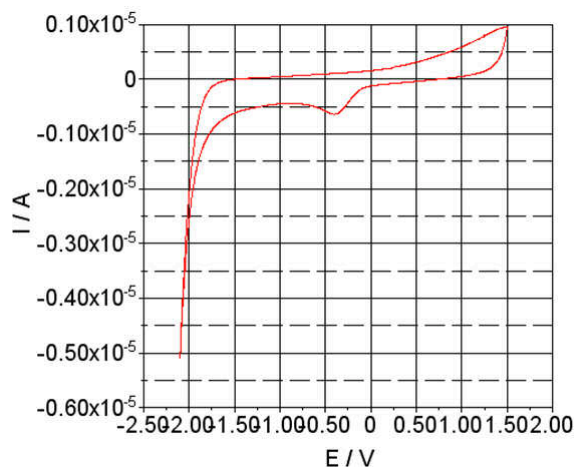


Fig. 1: Voltammogram of a 1M solution of LiClO₄ in PC at 0.01 V.s⁻¹

The impedance spectrum of a PMMA – LiClO₄ electrolyte is depicted for several potentials in Fig. 2 as an example. We can easily see that the spectrum consists essentially of a lowered semicircle caused by a pseudo capacity. An equivalent circuit as suggested in the experimental part can describe the low frequency part. Further, we can see rather small component at frequencies exceeding 1 kHz. This is supposed to correspond to the adsorption of the solvent and will be worth of further examination.

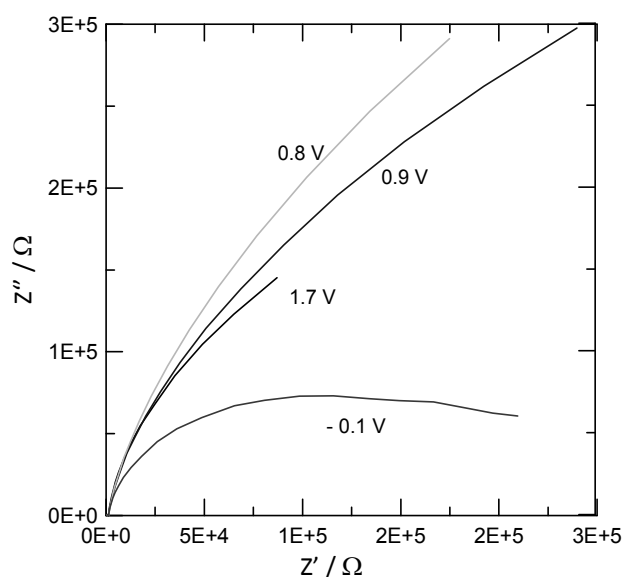


Fig. 2: Impedance spektrum at various potentials in 1M LiClO₄ in PC

The pseudo capacitance (the element C.P.E.) at various potentials in several inert salts is plotted in Fig. 3. Sodium, lithium, tetraalkylammonium and potassium – propylene carbonate electrolytes are compared.

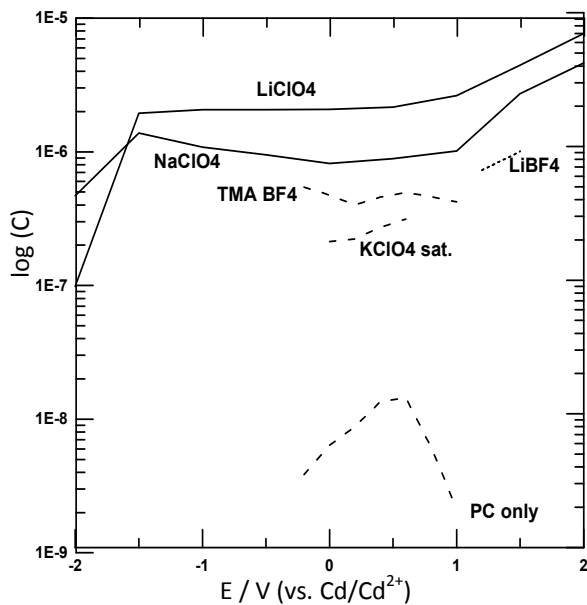


Fig. 3: Influence of electrolyte composition (given in the figure) on electrode capacitance

Apparently, the pseudo capacity passes through a minimum and at potential more negative. As the peak or wave corresponding to the SEI formation appears below -0.4 V, the impedance does no more correspond to the pseudocapacity model below that value (see Fig 4). Therefore, we restricted the investigation to the potentials from positive end to the range in which this phenomenon does not play any important role. As the exception, TEAClO₄ solution does not exhibit this effect.

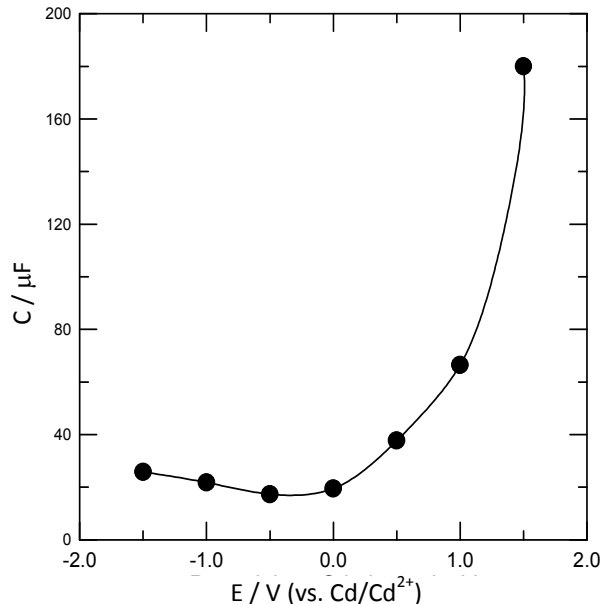


Fig. 4: The impedance of an electrolyte containing tetraalkylammonium perchlorate

The best results in the range of negative potentials were obtained with the solution if 1M TEAClO₄. We

see there the minimum of pseudo capacity at potentials in the vicinity of zero.

It should be noted that the KClO₄ solubility in PC are not very high and an almost saturated solvent (milimolar approx.) was used. Therefore, the capacitance is much lower in this case.

Further we can see the capacity found in pure PC. Its impedance is perhaps due to residual impurities or water content in PC.

The spectrum of LiClO₄ in gel polymer electrolyte is shown in following Fig 5. Two depressed semicircles are quite clear on the curves. The high frequency part is explained as the SEI layer on the interface, similar to those described on the lithium metal electrodes by Aurbach and coworkers [6].

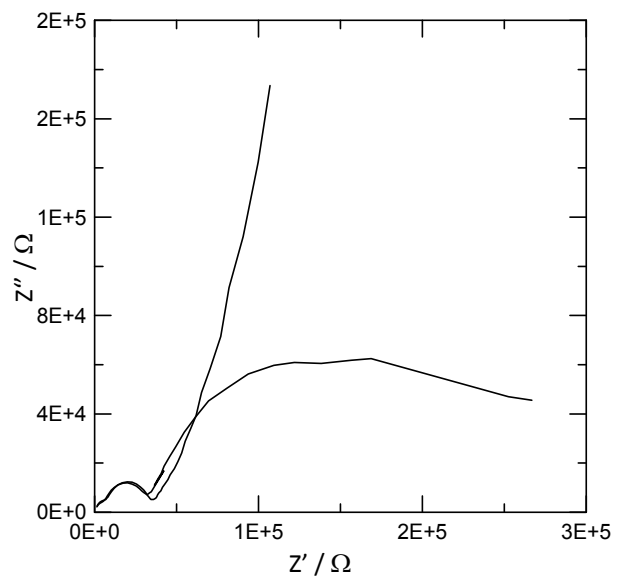


Fig. 5: Impedance in Li salt containing PMMA gel. Upper curve: potential 0.8 V, lower curve: potential 0 V (Vs. Cd/Cd²⁺ reference electrode)

CONCLUSION

In general, the capacity increases towards positive potentials and its value does differ much from those known in aqueous systems. This is not surprising as the relative permittivity of propylene carbonate (PC) is fairly high ($\epsilon = 64.4$). It is interesting that the highest capacity was found in the case of small lithium cations. Also the wide range of potentials accessible in tetraalkylammonium (TEA) salts indicates their importance in commercial supercapacitors.

The capacity in PC alone is by 2 - 3 orders of magnitude lower. The capacities should be inversely proportional to square root of concentration and such a result is in accordance with that presumption.

Further results will be oriented more towards the gel PMMA-PC based electrolytes and the use of various carbonaceous materials with large specific surface area.

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