

Electric Double Layer Structure at Porous Carbon Electrodes

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The electric double layer capacitors (EDLC) have been developed as the energy storage devices and are used for various applications. Desirable specifications (energy density, power density, discharge time *etc.*) of an EDLC depend on the characteristics of the porous electrode material as well as on the electrolyte properties [1]. Porous carbon with deep pores is an extreme example showing the influence of geometry of pores on the frequency dispersion of EDLC, and usually two types of distributed characteristics have been observed, created by the pore lengths longer than the penetration depth of *ac* signal, and by the pore size distribution in porous material [2]. Therefore the microstructure of a porous electrode and the electrolyte characteristics (conductivity, Debye screening length, adsorption free energy, *etc.*) should be optimized to obtain the optimal discharge time, desirable energy and power density. The main aim of this work was to study the influence of the electrolyte characteristics on the electric double layer parameters at the porous carbon electrodes.

Electric double layer structure on the porous carbon | x M (C₂H₅)₄NBF₄ + acetonitrile (AN) interface has been studied by the cyclic voltammetry and impedance measurement methods. The experimental details of an electrode preparation are given in [3]. Very pure AN (Aldrich) as well as TENBF₄ (Aldrich) have been used. Specific surface area, pore size distribution, micropore volume, micropore area and other parameters have been obtained according to the BET method. The concentration of TENBF₄ was varied from 5×10⁻³ M to 1.5 M solution. The aqueous saturated calomel electrode, connected with the measurement system through Luggin capillary and salt bridge system (0.01 M LiBF₄ in AN | 0.01 M LiBF₄ in H₂O) discussed in [4], has been used. According to experimental data the shape of Z', Z''-plots noticeably depend on the electrolyte concentration as well as on the electrode potential.

The complex plane plots for porous carbon | x M (C₂H₅)₄NBF₄ + AN interface can be divided into four sections. At a high *ac* permeability (i.e. at very low *ac* frequencies $f \leq 1 \times 10^{-1}$ Hz) the impedance behaves like a planar electrode since the penetration depth λ is larger than the length of a pore so that an *ac* signal detects very big amount of pore volume. In this *ac* frequency region the phase angle approaches to -90°, indicating to the so-called finite length effect, *i.e.* purely capacitance behaviour of porous material. However, the impedance shows non-ideal constant phase element (CPE) behaviour caused by the pore size distribution in the porous carbon material. However, in comparison with other carbon materials [1,2], the electrode material under discussion shows very narrow pore distribution, in good agreement with BET data. At higher *f*, the polarization depth is smaller and in Z', Z''-plots the so-called porous section with the phase angle value ~-45° has been observed. The length of porous section noticeably depends on the concentration of electrolyte and the pore resistance

increases with the dilution of electrolyte if $c_{el} \leq 1.0$ M. Between these regions a transition section has been established. At higher frequencies ($f > 50$ Hz), a very well expressed slightly depressed semicircle with the depression angle β somewhat higher than zero ($\beta = 0$ for purely heterogeneous adsorption or charge transfer reactions and $\beta = 45^\circ$ for diffusion limited stadium) indicate that the relaxation time $\tau_R = \omega_m^{-1}$ (ω_m – angular frequency at the maximum of Z', Z''-plot) corresponds to the kinetically mixed process [5]. τ_R increases with dilution of electrolyte. The high frequency value of Z' is practically independent of the concentration if $c_{el} \geq 0.1$ M, indicating that the electrolyte conductivity is not the only parameter obtaining the experimental serious resistance at $f \rightarrow \infty$.

Analysis of Z', Z''-plots indicates that the Paasch *et al.* model 1 [6], assuming that the two parallel conduction paths in the solid and liquid phases are interconnected by the electric double layer capacitance in parallel with the hindered charge transfer reaction (complex admittance), seems to be valid in our case. Analysis of Z', Z''-plots shows that in the region of frequencies $f \leq 1 \times 10^{-2}$ Hz the values of parallel and serious capacitances coincide, indicating that in the region of potentials $-1.4 < E < 1.4$ V (SCE), the carbon material under discussion is ideally polarizable. The limiting value of capacitance at $E \geq 0.7$ V is practically independent of c_{el} if $c_{el} \geq 0.1$ M. In the region of negative surface charge densities, C_s has maximum if $c_{el} \sim 0.1$ M.

Analysis of C_s, E -curves at $f \leq 0.1$ Hz (C_s is a serious resistance) obtained at different c_{el} shows that for dilute electrolyte solutions the very well expressed minimum with the potential E_{min} , practically independent of c_{org} as well as *ac* frequency ($f < 1 \times 10^{-1}$ Hz), can be seen. The capacitance C_{min} is practically independent of the potential scan direction as well as on the potential scan rate v ($v < 2$ mV s⁻¹) and therefore it seems that this minimum in C_s, E -curves is mainly caused by the diffuse layer characteristics and therefore $E_{min} = 0.27$ V (SCE) corresponds to the zero charge potential value of porous carbon | dilute (C₂H₅)₄NBF₄ + AN interface. With the rise of electrolyte concentration E_{min} shifts toward more positive values, indicating that (C₂H₅)₄N⁺ cations are more surface active than BF₄⁻ anions. Thus, at $c_{el} \geq 0.1$ M the dependence of E_{min} on c_{el} can be explained by the specific adsorption of (C₂H₅)₄N⁺ cations on the porous carbon electrodes.

References

1. B.E. Conway, *Electrochemical Supercapacitors. Scientific Principles and Technological Applications*, Kluwer – Plenum, New York, 1999.
2. H.–K. Song, Y.–H. Jung, R.–H. Lee, L.H. Dao, *Electrochim. Acta* **44**, 3513 (1999).
3. M. Arulepp, A. Jänes, G. Nurk, L. Permann, P. Nigu, E. Lust, Abstracts of 51st Ann. ISE Meeting, Warsaw, Poland.
4. S. Trasatti, E. Lust, *Modern Aspects of Electrochem.*, Vol. 33, Kluwer Academic / Plenum Publishers, New York and London, 1999, p. 1.
5. J.R. Macdonald, *Impedance Spectroscopy*, Wiley, New York, 1987.
6. G. Paasch, K. Micka and P. Gersdorf, *EA* **38**, 2653 (1993).