DOUBLE LAYER ON CARBON IN APROTIC ELECTROLYTES

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Introduction

One of most important phenomenons in electrochemistry is the double layer which exists on the boundary between an electronically conductive electrode and an ionic conductor, called electrolyte.

For many reasons, the importance of non – aqueous electrolytes has been increasing permanently in recent two or thee decades. An extended application field is the electrochemistry of lithium batteries, electrochromics and electrochemical supercapacitors.

The phase boundary between electrode and electrolyte depends on the nature of electrochemical properties of both entities. Essentially, we have to consider whether any chemical reaction proceeds on the boundary or not. The latter case is called "polarized boundary" in classical electrochemistry or "blocking boundary" in the ectrochemistry of solid electrolytes.

As aprotic electrolyte, we shall understand either liquid or gelous polymeric system which does not contain any "acidic" hydrogen atoms which could be converted into quasifree hydrogen cations. For any theoretical investigation we should start with a completely inactive electrode. From application reasons we started to study various carbonaceous materials and propylene carbonate based liquid or gelous electrolytes.

Let us imagine a infinite planar boundary of an ideally conductive electrode and an electrolyte. The potential inside the electrolyte we denote as Ψ and we suppose its dependence on the distance $\underline{x}$ from the boundary. If no electrochemical reaction occurs, *i.e.*, if no *d.c.* current is flowing acreoss the boundary, then a space charge region is formed by the action of electrostatic forces. Then the well known Poisson equation describes the distribution of potential as follows:

$$\frac{\partial^2\Psi}{\partial x^2} = \frac{e_0\rho}{\varepsilon\varepsilon^0}.$$

$$\rho(x) = \rho_\infty.\exp\left(\frac{e_0.\Psi}{k.T}\right)$$

Thus, the distribution of potential can be obtained by a two – fold integration of the effective concentration of free charges ρ and the total charge Q is accessible in this way. Finally, we can define the differential capacity $C_{dif} = dQ/d\Psi$. It should be noted that this quantity is strongly dependent on the potential and can be regarded as non) linear capacity.

Two essentially different cases may occur:

a) Only one kind of ions is free, while the counterions are firmly bound to the quasisolid or solid structure of the electrolyte. This behavior is observed in solid and ion exchanging membranes. Then the method of calculation and its results are quite similar to that of Schottky junction of metal and semniconductor including a marked asymmetry of the voltage – to – capacity profile.
b) On contrary, we have both positive and negative ions free in liquid systems and the equations are more complex. The differential capacitu passes through a minimum at potential at which the space charge just disappears; this potential is called “potential of zero charge”.

Let us mention, that it was just the study of double layer on boundary between water and mercury which lead Professor Heyrovský to the discovery of polarography as the basic discovery of modern electrochemistry.

Unfortunately, the behavior of a system electrode – electrolyte is rather complex sometimes. Following phenomenons has been known until now:

a) specific adsorption (as monomolecular layers mostly) of various ions is potential dependent and kt ks connected wjth a voltage dependent charge, *i.e.,* as “pseudocapacity” in series with the capacity of the space charge.
b) A layer either of low conductivity or possessing ionic conductivity may be formed on the interface. For example,a layer containing $LiCO_3$ and some badly defined polymers is formed from propylene carbonate, mainly in the presence of water in very small traces. Alsi the impedance of this layer is in series with the impedance of the space charge.
c) The electrode – electrolyte system is not absolutely non – reactive. Then a background *d.c.*current flous and is in parallel to the impedance of the double layer.

Experimental

As carbonaceous materials we started with glassy carbon electrodes and continued to use variety pf carbon black powders, carbon nanotubes and chemically modified graphite in powderized form. Solutions of alkali metal and tetraalkylammonium salts in propylene carbonate and other aprotic solvents were used both as liquid electrolytes and as the ionic components of PMMA based gels.

Cyclic voltammetry and impedance spectroscopy were used for the evaluation of electrode capacities. The impedance spectrums were deciphered using Boucamp program.

Three electrode arrangement and potentiostats were used for all investigations.

Even traces of water had to be removed from all systems, otherwise the results would be strongly distorted.

Examples of results

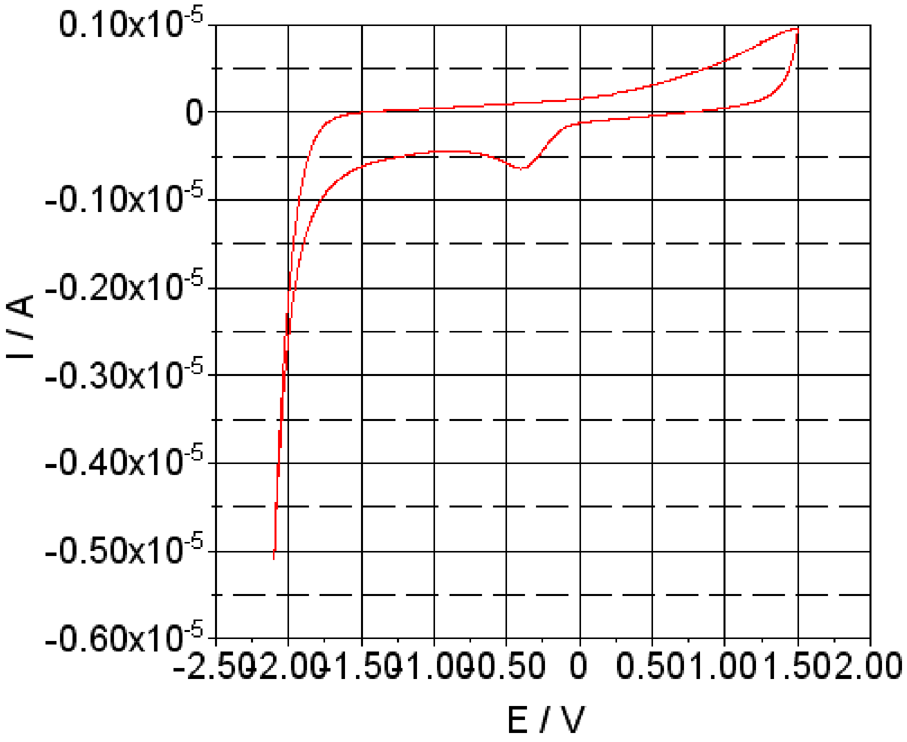
The voltammetry of a glassy carbon electrode in $LiClO_4$/ PC is shown in here.

Also an impedance spectrum can be given in following picture.

Finally, the capacitance element in impedance spectrum is dependent on potential as is given here.

For technological reasons we have investigated the possibility to prepare a carbonaceous layer containing graphite powder, a binder and a substance which creates macroscopic pores in the mass.

The impedance of a glassy carbon in gel polymer electrolytes is rather complex. Examples will be shown. The impedance spectrum and the width of voltammograms correspond to capacity in the range of 10 μF / cm^2.



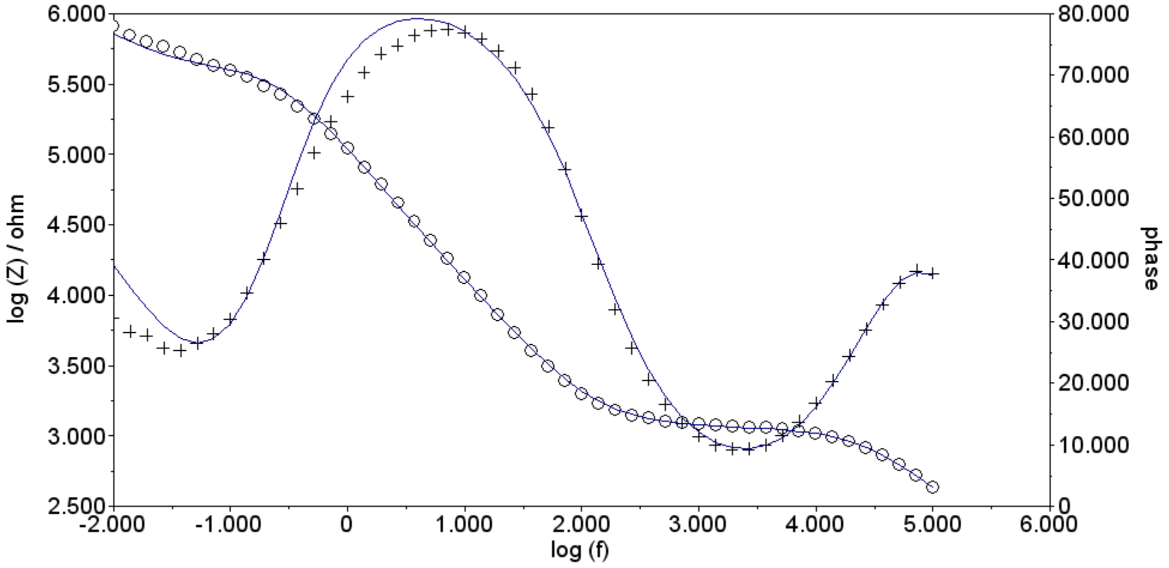


Fig. 1 and Fig. 2 *Voltammetry and impedance spectrum of a glassy carbon electrode in* $LiClO_4$ *electrolyte*

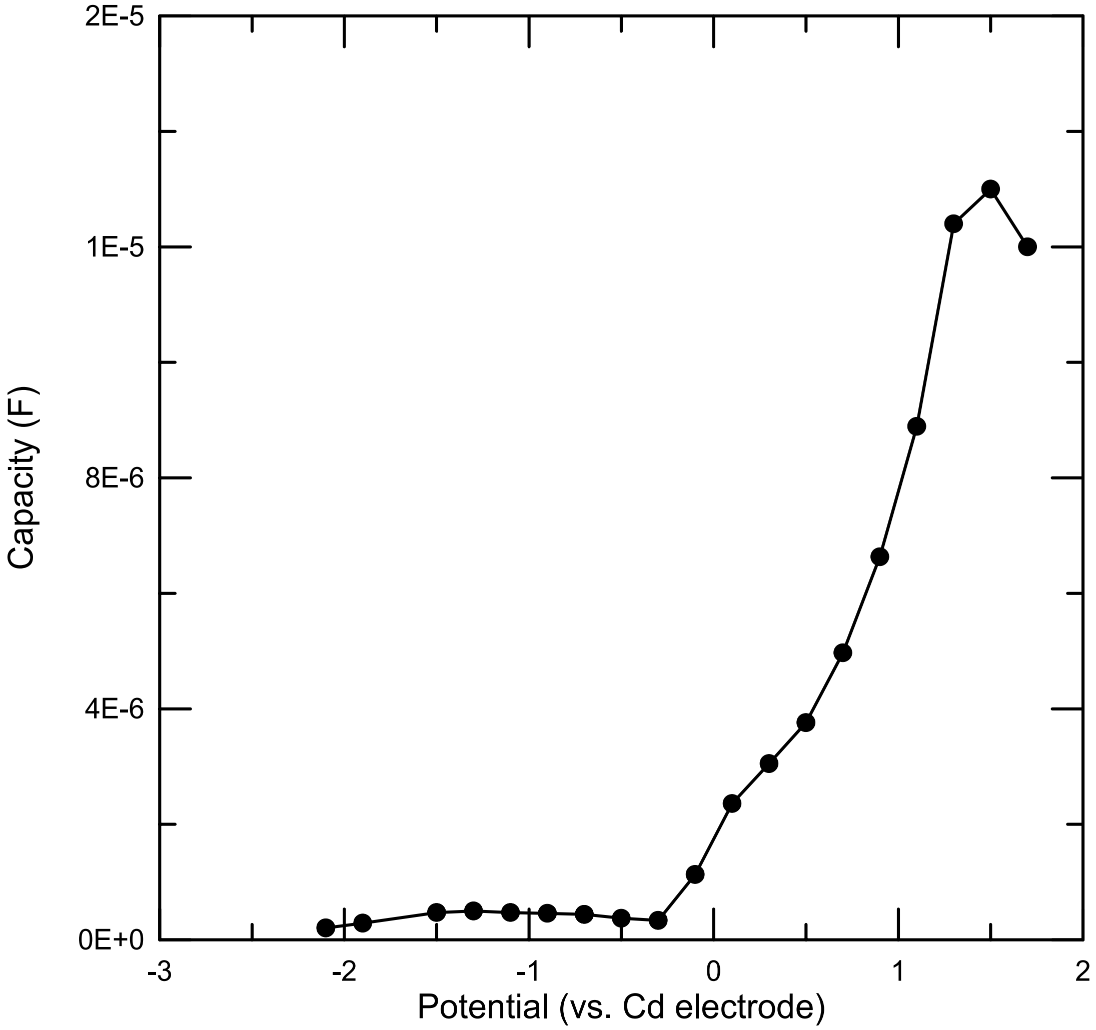


Fig. 3 *The double layer capacity of a glassy carbon in liquid* $LiClO_4$ *– PC electrolyte*

The lof apparent capacity below 0 V is caused by a formation of a badly conducting film on the electrode from PC reduction.

Supercapacitors – a technological application

The principle of double layer on carbon electrode has been used for the design of new components, called electrochemical supercapacitors.

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