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Vasyl StefanykPrecarpathian
National University

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I.M. Budzuliak, L.S.Yablon, V.O. Kotsyubynsky, B.I. Rachii, I.I. Budzuliak,
V.M. Boychuk, R.V. Ilnytskyi, R.I. Kryvulych

Interaction of electrolyte molecules with the surface of porous carbon: NMR study

Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukraine, volodymyr.kotsuybynsky@pnu.edu.ua

Electrochemical double-layer capacitors use porous carbons as the electrode material, and improving their performance requires an understanding of the electrolyte−carbon surface interactions. ^{13}C, ^{14}N, and ^{11}B NMR spectroscopy were used to investigate the behaviour of the $[C(OCH3)_3NH_3]^+Cl^-$ and $[N(CH_2CH_3)]^+BF_4^-$ electrolytes on the surface of porous carbon in D_2O solutions. A chemical shift of ^{13}C has been found for the N–C bond indicating electron density redistribution between nitrogen atoms and alkyl fragments. The presence of a signal with a chemical shift of $\delta = 7.7$ confirms the structuring of the electrolytic layer of water solution $[N(CH_2CH_3)]^+BF_4^-$.

Keywords: porous carbon, NMR, chemical shift, electrolyte.

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Introduction

The electric double layer (EDL), which forms at the boundary between the electrode material and the electrolyte, serves as the functional basis of charge / discharge capacitor devices. This underlines the importance of understanding the behaviour of the electrolyte on the electrode material surface. According to Conway's definition [1], electrochemical systems characterized by ongoing quasi-reversible charge-discharge processes and charge-discharge curves close to linear are called electrochemical capacitors (ECs). Their capacitance is determined by the EDL formed at the solid−electrolyte interface. Such capacitors exhibit relatively high specific energy characteristics and are widely used in electronics and electrical engineering devices, such as autonomous power supply systems, power amplification cascades of solar cells, and internal combustion engine start-up systems, among others.

The formation of the electric double layer occurs at the interfacial boundary between two media with different types of conductivity: electronic and ionic. As chemical potentials equalise upon reaching equilibrium, charges of opposite signs accumulate in the contact areas of each phase: electrolyte ions and electrons (or holes) in the solid body. Physical contact between these media leads to the formation of the electric double layer. The charges in EDL are localized at a short distance, with the thickness of the EDL in a range of 4-7 Å [2].

The condition of electrical neutrality implies that in the equilibrium state the charges on different sides of the EDL are equal. By introducing the concept of volume charge polarisation as capturing of charge carriers at the interfacial boundary due to the impossibility of their free discharge or charge carriers exchange on the electrodes, we come to understand the operational mechanism of such capacitors – it is the polarisation (or depolarisation) of the EDL volume charge when an external potential difference is applied to the capacitor covers. The process of polarisation corresponds to the EC charging when electrons from the solid phase side and electrolyte ions will be concentrated on the EDL covers, and the depolarization process – EC is discharged accordingly. From the above, it follows that not every EDL can satisfy the conditions for the construction of an EC, since it is necessary to create conditions that would ensure reliable spatial separation of charges and polarisation of the volume charge. During electrode polarisation, Faraday processes associated with mass transfer across the phase interface do not occur on the electrode, which would otherwise completely prevent charge transfer processes. Therefore, such electrodes are also called blocking electrodes. Under these conditions, the contacting phases will not exchange charges, and all the energy of the external electric field will be spent on charging the EDL. Then in the galvanostatic mode, within the scope of "ideal polarisability" potential, we obtain a linear dependence of the voltage on the duration of the polarisation process, from which the capacitance of the EDL is expressed as $C = \frac{\Delta q}{\Delta U} \sim \frac{S}{D}$, where Δq is the charge, ΔU is the change in the potential difference during the transfer of the charge Δq; S and d are the electrode surface active area and the EDL thickness, respectively.

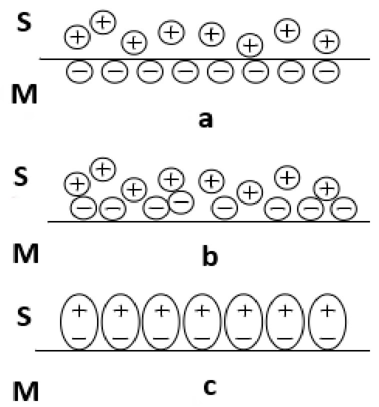

Fig. 1. Schematic diagram of the EDL: a – ionic; b – adsorptive; c – orientational; S – solution; M – metal.

The interfacial boundary at the blocking electrodes restricts the transport of electric charge carriers. The physical nature of this phenomenon is as follows: the EDL formation process is caused by specific adsorption, surface phenomena, etc., but not by charge transfer across the boundary itself. Thus, an EDL on blocking electrodes can be described as a molecular capacitor with electric charges on its "covers" that arise from the redistribution of electrons or charged point defects in the solid and electrolyte ions. Its capacitance can be represented as $C = \varepsilon\varepsilon_0 S/d$, where ε is the dielectric permittivity of the Helmholtz layer, which is often confused with the dielectric permittivity of the electrolyte (its solvent). Since the thickness of the EDL d is small (a few interatomic distances), it provides a high capacitance per surface unit (about 20–50 μF/cm^2), which is significantly higher than the corresponding value in traditional capacitors, where the dielectric thickness is 500-700 interatomic distances.

An EDL is formed between two phases of different physical origins: metal / electrolyte solution, solid dielectric / liquid dielectric, and metal / solid electrolyte. The most efficient charge separation is provided by the EDLs that emerge on the surfaces of metal electrodes immersed in an electrolyte solution. Charge separation can be caused by various reasons (Fig. 1): a) by the transition of ions from the electrode to the solution or vice versa – ionic EDL; the charge of one sign is formed by the ions that have passed into the solution, and the remaining ions (electrons) form a charge of the opposite sign; b) by specific adsorption of ions of the same sign on the electrode surface – adsorptive EDL; c) by the orientation of polar molecules (e.g., solvent molecules) near the electrode surface, when all molecules are oriented towards the electrode with the same side – orientation EDL. Usually, different types of EDL occur simultaneously. It should be noted that in all of these cases, the EDL remains electrically neutral. An important component that determines the efficiency of electric energy sources and accumulators is the electrolyte type (aqueous or aprotic), the properties of which depend on the solvent composition, the nature and concentration of alkali, acid, or salt [3].

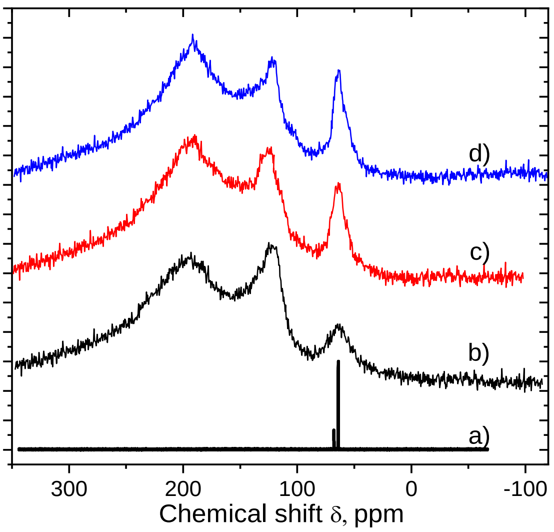

Fig. 2.^{13}C NMR spectra of $[C(OCH_3)_3NH_3]^+Cl^- + D_2O$ (a), PCM+$[C(OCH_3)_3NH_3]^+Cl^- + D_2O$ (b), PCM+Mn+$[C(OCH_3)_3NH_3]^+Cl^- + D_2O$ (c), and PCM+Mn+Las+$[C(OCH_3)_3NH_3]^+Cl^- + D_2O$ (d).

Mixtures of two or three lithium salt solvents, such as Li_2SO_4, $LiClO_4$, $LiPF_6$, $LiN(CF_3SO_3)_2$, $LiCF_3SO_3$, and $LiBF_4$, are predominantly used for the lithium-ion power sources [4]. Organic electrolytes are commonly used in the production of capacitors since they make it possible to achieve high operating voltage (up to 5.7 V). Organic electrolytes for electrochemical (EC) applications require salts, such as perchlorates, tetrafluoroborates, and hexafluorophosphates, dissolved in aprotic organic solvents, such as propylene carbonate, tetrahydrofuran, γ-butyrolactone, acetonitrile, among others. These electrolytes play a crucial role in the symmetry of the anode-cathode processes and prevent the introduction of highly active alkaline cations into the electrode structure, thereby maintaining the integrity of the double-layer capacitor (DLC) structure. To enhance the performance and stability of the electrolyte, it is advantageous to use salts with large cation-anion parts. For instance, salts containing tetraethylammonium cations paired with hexafluorophosphate or tetrafluoroborate anions are promising. This choice helps to minimise the risk of structural distortions in the electrolyte, providing better electrochemical performance and stability.

I. Experimental details

Sample preparation

A mixture of crushed apricot stones and water (mass ratio of approximately 1:1) was placed in a stainless-steel autoclave and carbonised at 800 °C. The conditions of the carbonisation procedure were based on previous studies [2]. For chemical activation, KOH, carbon, and water in a1:1:1 mass ratio were stirred for 1 hour and dried at 110°C, followed by thermal treatment at 600°C in an inert atmosphere for 1 hour. The carbon was washed to pH = 6.0, dried, and ground to a fraction of 100 μm. For carbon doping, potassium permanganate $KMnO_4$ with Mn ions in oxidation state +7 was used. An aqueous solution (5%) of $KMnO_4$ (100 mL) was mixed with ethyl alcohol (6.5 mL) and HNO_3 (5 mL) under heating to 80°C. The precipitate was washed, dried at 100°C, dissolved in water, and mixed with carbon. After stirring for 5 hours and drying at 120°C, carbon was obtained with the expected content of Mn ions 2 wt.%.

Material characterisation

^{13}C, ^{14}N, and ^{11}B nuclear magnetic resonance spectra were obtained using a Bruker AVANCE 400 spectrometer (magnetic field 9.39 T, frequency 400 MHz).

II. Results and discussion

NMR spectroscopy allows us to distinguish between different molecular species present in the electrolyte and at the electrode-electrolyte interface and to understand the reaction mechanisms [5]. The ^{13}C, ^{14}N and ^{11}B NMR spectra of the polyfunctional electrolytes $[C(OCH_3)_3NH_3]^+Cl^-$ and $[N(CH_2CH_3)]^+BF_4$ in D_2O solutions were studied. The solutions for measuring the NMR spectra had the same concentration, which makes it possible to quantify the results and to correct the juxtaposition of the spectra in terms of the redistribution of components by their state. Characteristic lines are observed in the NMR spectra of the electrolyte solutions (Fig. 2-3, Fig. 4 and Fig. 4), parameters of the NMR spectra are presented in Table 1. Liquid samples are usually used for ^{13}C NMR spectroscopy (natural content of ^{13}C carbon is 1.1%, NMR effect efficiency is about 1.07%) due to the significant broadening of spectral lines for solid samples. During the interaction of the electrolyte and the surface a near-surface layer is formed, where the mobility of fragments or molecules increases, causing observable narrowing of the lines. Indeed, two lines are observed in the NMR spectrum of the original PCM

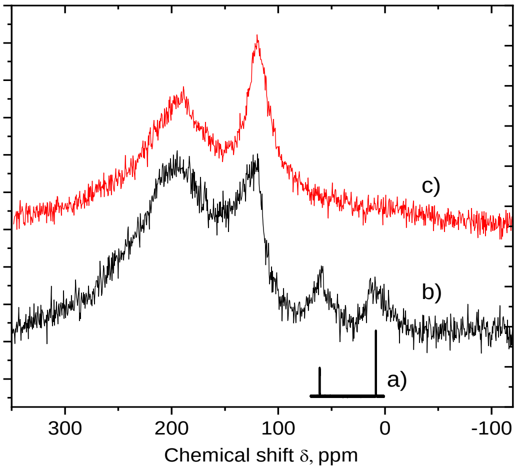

Fig. 3. ^{13}C NMR spectra of $[N(CH_2CH_3)]^+BF_4^-+D_2O$ (a), PCM+$[N(CH_2CH_3)]^+BF_4^-$+ D_2O (b), and PCM+ D_2O (c).

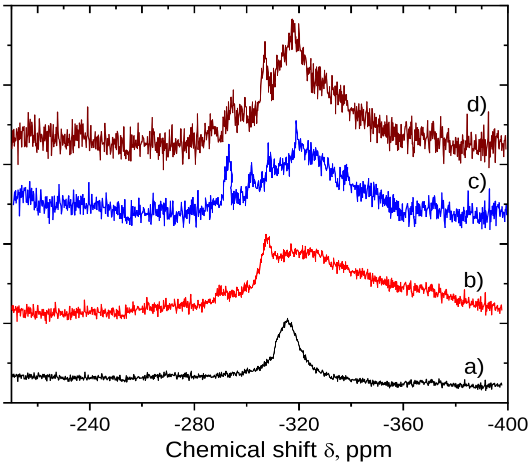

Fig. 4. ^{14}N NMR spectra of $[C(OCH_3)_3NH_3]^+Cl^-+D_2O$ (a), PCM+$[C(OCH_3)_3NH_3]^+Cl^-$+ D_2O (b), PCM+Mn+$[C(OCH_3)_3NH_3]^+Cl^-$+ D_2O (c), and PCM+Mn+ $[C(OCH_3)_3NH_3]^+Cl^-$+ D_2O (d).

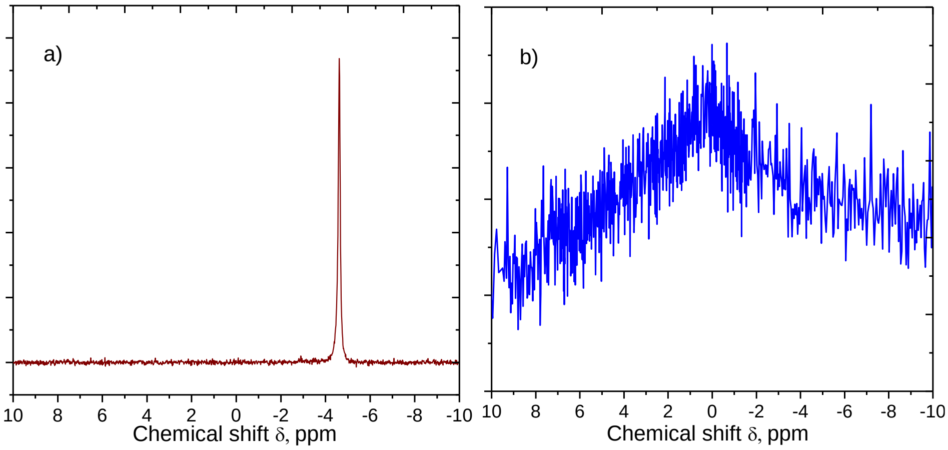

Fig. 5.^{11}B NMR spectra of NMR spectra of $[N(CH_2CH_3)]^+BF_4^-+D_2O$ (a) and PCM+$[N(CH_2CH_3)]^+BF_4^-$+ D_2O (b).

Table 1.

^{13}C, ^{14}N and ^{11}B NMR chemical shifts and line widths of electrolytes, porous carbon (PCM) loaded with 1M $[C(OCH_3)_3NH_3]^+Cl^-$ or 1M $[N(CH_2CH_3)]^+BF_4^-$ in D_2O and PCM in D_2O

Sample	^{13}C		^{14}N		^{11}B	
	chemical shift δ, ppm	Δν, Hz	chemical shift δ, ppm	Δν, Hz	chemical shift δ, ppm	Δν, Hz
$[C(OCH_3)_3NH_3]^+Cl^-+D_2O$	61.7	0.05	-315.9	8.8	-	-
	63.9	0.06	-	-	-	-
$PCM+[C(OCH_3)_3NH_3]^+Cl^-+D_2O$	62.7	19	-320	34	-	-
	122.7	31	-307	4	-	-
	196.9	66	-	-	-	-
$PCM+Mn+[C(OCH_3)_3NH_3]^+Cl^-+D_2O$	63.1	13	322	35	-	-
	122.9	28	-	-	-	-
	195.1	68	-	-	-	-
$PCM+Mn+[C(OCH_3)_3NH_3]^+Cl^-+D_2O$	63.2	13	317	33	-	-
	122.5	26	-	-	-	-
	192.0	70	-	-	-	-
$[N(CH_2CH_3)]^+BF_4^-+D_2O$	8.3	0.03	-	-	-4.5	0.6
	53.7	0.01	-	-	-1.3	6
$PCM+[N(CH_2CH_3)]^+BF_4^-+D_2O$	7.7	26	-	-	-	-
	58.6	14	-	-	-	-
	120.6	18	-	-	-	-
	127.5	20	-	-	-	-
	183	36	-	-	-	-
	198	50	-	-	-	-
$PCM+D_2O$	118.5	28	-	-	-	-
	188.5	79	-	-	-	-

matrix in D_2O (Fig.3). The observed lines corresponds carboxyl groups and chains with conjugated carbon-carbon bonds (presence of unsaturated carbon-containing fragments characterised by both σ- and π-bonds): carboxyl groups- polyconjugated chains. The ^{13}C NMR spectra of the $PCM+[N(CH_2CH_3)]^+BF_4^-+D_2O$ composition are characterised by similar changes compared to those of the starting components.

The line broadening indicates a steric (spatial) restriction of the freedom degrees of molecular mobility. The effect of line broadening is also partially the result of the influence of an internal magnetic field created by unpaired electrons detected by EPR. The change in the chemical shift in the ^{13}C nuclei of N-C bonds indicates a redistribution of the electron density between nitrogen atoms and alkyl fragments (and possibly the counter-ion). The change in the values of chemical shifts indicates a change in the types of associates (ion-ion, ion-molecular) formed by tetraethylammonium cations in the surface layer compared to the original solution. The detection of a signal with $\delta = 7.7$ ppm indicates a variety of forms of associates and types of interaction in the near-surface layer. Another confirmation of the structuring of the electrolytic near-surface layer is the result of comparing the ^{11}B NMR spectra of the initial solution and the PCM+electrolyte composition (Fig. 5). The broadening of the ^{11}B line indicates a significant decrease in the symmetry of the anions from the tetrahedron, which is possible only with the near-surface layer association and structuring [6].

The change in the ratio of integral intensities and line widths of PCM+electrolyte NMR spectra in the regions of $\delta = 127.5$ and $\delta = 198$ indicates that chains with conjugated bonds are involved in the structures formed in the near-surface with the participation of electrolyte layer, along with carboxyl groups [7]. However, the involvement in this interaction is incomplete, since the decomposition of the lines into separate components indicates the presence of fragments that retain their characteristics, as in the PCM + water system [8]. When the electrolyte+D_2O solution comes into contact with the PCM surface, the molecular mobility of electrolyte cations also changes (Fig. 3). Switching to the manganese-modified composition, the ^{13}C NMR line δ= 62.7 ppm narrows, that is explained by decreasing in the concentration of paramagnetic centres, which correlates with a change in the intensity of the corresponding EPR signals of the samples. The change in the ratio of the integral intensities of the ^{13}C NMR spectrum lines of the manganese-modified samples before and after pulsed laser irradiation may indicate a change in the nature of fractal near-surface chains [9], which is confirmed by the ^{14}N NMR spectra (Fig. 4).

Conclusion

The NMR spectra of the $PCM+[N(CH_2CH_3)]^+BF_4^-+D_2O$ composition revealed the presence of carboxyl groups and chains with conjugated σ- and π-carbon–carbon bonds in the carbon lines. The broadening of the lines indicates steric (spatial) restriction in freedom degrees of molecular mobility. This broadening is also attributed to the influence of the internal magnetic field generated by unpaired electrons. The signal with δ=7.7 ppm indicates the structuring of the electrolytic surface layer. The observed line broadening indicates a significant decrease in the symmetry of the anion tetrahedrons, which typically occurs only in the case of association and structuring of the near-surface layer.

Budzulyak I.M.–Professor, Doctor of Physical and Mathematical Sciences;
Yablon L.S.–Professor, Doctor of Physical and Mathematical Sciences;
Kotsyubynsky V.O. –Professor, Doctor of Physical and Mathematical Sciences;
Rachiy B.I.–Professor, Doctor of Physical and Mathematical Sciences;
Budzulyak I.I.–PhD student;
Boychuk V.M. – Professor, Doctor of Physical and Mathematical Sciences;
Ilnytskyi R.V.–Professor, Doctor of Physical and Mathematical Sciences;
Kryvulych R.I.–PhD student.

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І.М. Будзуляк, Л.С. Яблонь, В.О. Коцюбинський, Б.І. Рачій, І.І. Будзуляк,
В.М. Бойчук, Р.В. Ільницький, Р.І. Кривулич

Взаємодія молекул електроліту з поверхнею пористого вуглецю: ЯМР дослідження

Прикарпатський національний університет імені Василя Стефаника, Івано-Франківськ, Україна,
volodymyr.kotsuybynsky@pnu.edu.ua

Електрохімічні конденсатори подвійного електричного шару використовують пористий вуглець як електродний матеріал, і покращення їхньої роботи вимагає розуміння взаємодії поверхні вуглецю та електроліту. Методами ЯМР ^{13}C, ^{14}N і ^{11}B вивчено поведінку електролітів $[C(OCH_3)_3NH_3]^+Cl^-$ і $[N(CH_2CH_3)]^+BF_4^-$ на поверхні пористого вуглецю в розчинах D_2O. У фрагментах N–C виявлено хімічний зсув ^{13}C, що свідчить про перерозподіл електронної густини між атомами азоту та алкільними фрагментами. Наявність сигналу з хімічним зсувом δ = 7,7 є доказом структурування частинок електроліту $[N(CH_2CH_3)]^+BF_4^-$ поблизу поверхні вуглецю в D_2O.

Ключові слова: конденсатор подвійного електричного шару, ЯМР, пористий вуглець, електроліт.