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Advanced analytical techniques to characterize materials for electrochemical capacitors

Zifeng Lin^{1,2}, Pierre-Louis Taberna^{1,2} and Patrice Simon^{1,2,3,*}

This review covers recent developments in advanced analytical techniques to characterize materials for electrochemical capacitors. For double layer capacitors, examples of the use of *in situ* X-ray photoelectron spectroscopy (XPS), pulsed electrochemical mass spectrometry (PEMS) technique, temperature-programmed desorption coupled with mass spectrometry (TPD-MS) technique, *in situ* NMR spectroscopy, and *in situ* dilatometry measurement are presented, for studying carbon/electrolyte interface with a focus onto electrolyte ions confinement in nanopores and changes during ageing. For the pseudocapacitive system, *in situ* X-ray (neutron) diffraction or scattering, *in situ* dilatometry technique, cavity micro-electrode, *in situ* Raman spectroscopy, TPD-MS technique, and electrochemical quartz crystal microbalance (EQCM) technique have been employed for studying materials structure, electrochemical kinetic, interface interaction, and ions adsorption/desorption. These advanced analytical techniques probe insight into charge storage mechanisms, and guiding the fast development of supercapacitors.

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Introduction

During the past 15 years, major scientific advances have been made in the field of Electrochemical Capacitors (ECs) which led to a 2-fold increase of the energy density of carbon-based (EDLCs) or to the development of high-rate pseudocapacitive materials. These advances

have been mainly achieved thanks to the use of analytical techniques, used in combination with *in situ* electrochemical conventional methods and/or with modeling. In this review, some advanced techniques, as well as their roles in studying charge storage mechanisms are introduced.

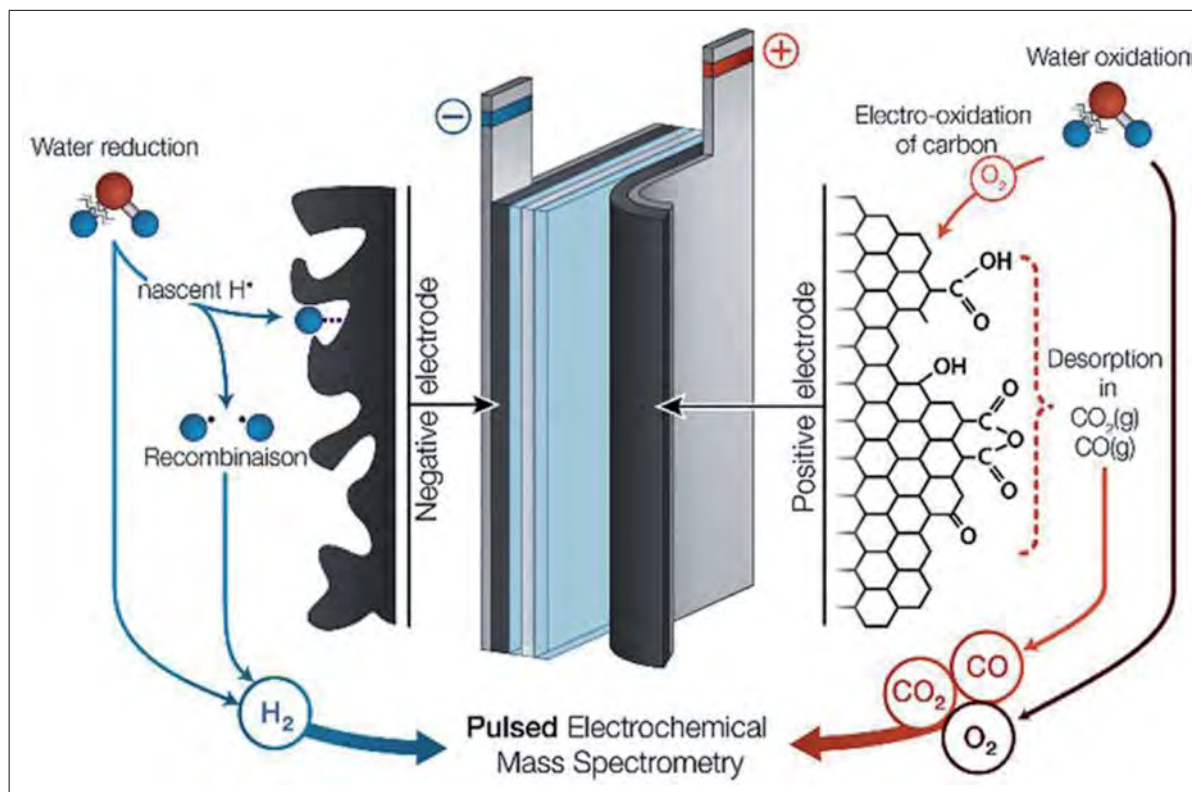
Electrochemical double layer capacitors

In Electrical Double Layer Capacitors (EDLCs), capacitive storage is achieved through ion adsorption of an electrolyte onto high surface area porous carbon electrodes [1]. Then, most of the electrochemical process in EDLCs occurs at the carbon/electrolyte interface. The analytical techniques used in EDLCs mainly focus on this interface.

One of the important parameters of ECs is the operating voltage window, which drives the energy density of the system. *In situ* X-ray Photoelectron Spectroscopy (XPS) technique has been used to study the stability of the carbon/electrolyte interface during electrochemical polarization of CDC carbons in ionic liquid electrolyte [2,3]. By tracking the change in the C1s and N1s energy levels, Lust and co-workers identified the reaction mechanism responsible for the electrolyte degradation at high potential (>3.6 V), which involves the oxidative dimerization of the imidazolium cation via N–N bond formation [2]. Another technique recently developed for monitoring gas evolution during the operation of supercapacitors is the pulsed electrochemical mass spectrometry (PEMS) technique [4*], as presented in Figure 1. PEMS technique allows for fast quantitative measurement of low gas production during supercapacitor cycling or ageing. Batisse and Raymundo [4*] evidenced and quantified the formation of CO, CO₂ and H₂ at the positive and negative electrode during supercapacitor cells ageing at constant voltages in aqueous electrolytes. Furthermore, they could correlate gas production to the change of each electrode potential versus reference during ageing. Ageing mechanisms in porous carbon electrodes strongly depend on the presence of surface functional groups on the carbon surface, as well as the carbon structure (presence of defects) and texture (surface area and pore size distribution). Here also, many advances have been achieved within the past 10 years.

A key technique for analyzing the carbon surface is the temperature-programmed desorption coupled with mass spectrometry (TPD-MS) technique [4*–7]. TPD-MS technique allows for measuring the surface group nature and content as well as the active surface area (ASA)

Figure 1



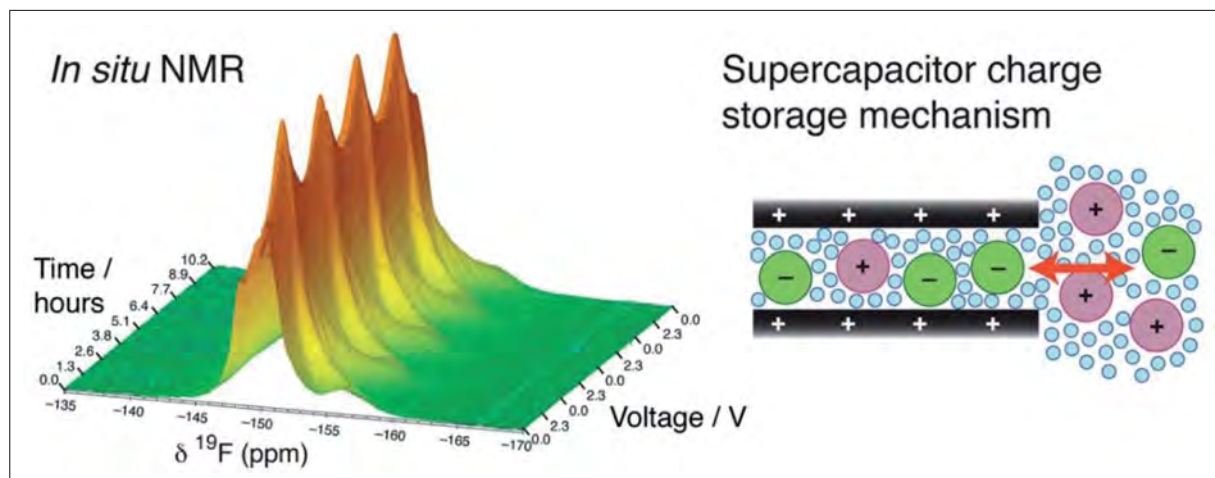
Observation of gas evolution at electrode/electrolyte interface by a modified pulsed electrochemical mass spectrometry (PEMS) method. Adapted with permission from ref. [4^{*}]. Copyright© 2017 American Chemical Society.

which accounts for the presence of carbon active sites: defects such as dislocations, stacking faults or atom vacancies mainly located in the edge planes [7]. Using carbon onions with controlled defect and surface group contents as model materials, a direct correlation was reported between the number of defects on the carbon surface measured by TPD-MS and the capacitance in both aqueous and non-aqueous electrolytes. Surprisingly, the contribution of the surface defects to the capacitance was found to be higher than that of the functional surface groups, even in aqueous electrolytes. These results show that the surface defects content also affects the carbon capacitance.

Besides the carbon structure and surface group content, the electrochemical performances of porous carbons are also controlled by the carbon texture: specific surface area, pore volume, pore size, pore size distribution. Back to 15 years ago, the carbon-specific surface area SSA was mainly calculated from N₂ gas sorption isotherms at 77 K using the Brunauer–Emmett–Teller (BET) equation. The evidence of the capacitance increase in carbon pores less than 1 nm [8–10] highlighted the need for refining the characterization methods to finely measure the porous volume and pore size in the ultra-microporous range (<1 nm).

Following recommendations of the IUPAC, the BET equation is not suitable for the measurement of specific surface area of microporous carbons [11]. Instead, for microporosity assessment, CO₂ sorption at 273 K should be preferred to alleviate kinetics restrictions observed during measurements at low temperature with (77 K with N₂) [11]. In the same way, calculation of the SSA using quenched solid density functional theory (QS-DFT) avoids the fundamental limitations of the BET theory [12]. Finally, the porous volume accessible to ions should be considered, that is the porous volume of pores larger than the size of the desolvated ion [13]. Based on the previous recommendations, Jäckel *et al.* [13] propose to use CO₂ gas for measuring porous volume below 0.9 nm and N₂ gas for pores > 0.9 nm. The change of the capacitance normalized to QS-DFT SSA versus accessible pore size shows a capacitance increase in pores less than 1 nm size for various porous carbons in non-aqueous electrolytes (in acetonitrile- or propylene carbonate-based electrolyte). Initially reported in 2006 using a series of porous carbons with controlled pore size [10], the origin of the capacitance increase in carbon nanopores has been extensively studied since that time mainly by using new or advanced *in situ* techniques. Beyond the capacitance increase, the

Figure 2



In situ NMR spectroscopy experiments carried out at different charge states allow quantification of the number of charges storing species. Adapted with permission from ref. [15]. Copyright © 2013 American Chemical Society.

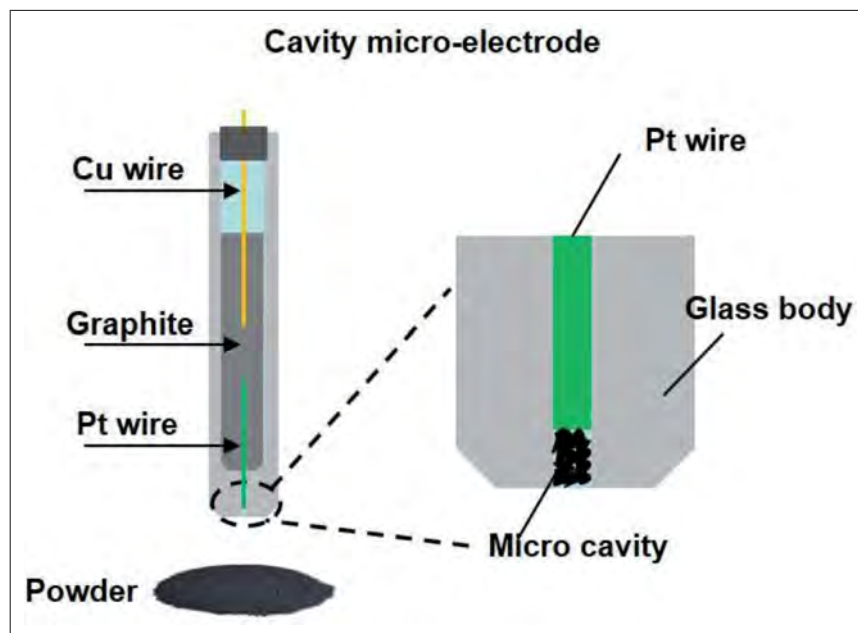
work was directed toward the understanding of the ion transport and adsorption in confined carbon nanopores (<1 nm), i.e. where there is no room for the building of a diffuse layer. *In situ* NMR spectroscopy experiments during electrochemical polarization of porous carbons in NaF aqueous electrolyte have shown that ions could access subnanometer pores with partial anion dehydration under polarization [14]. Using dedicated electrochemical cell, as shown in Figure 2, *in situ* NMR experiments during polarization also evidenced different charge storage mechanisms depending on the electrode polarity [15–19**]. Counter ion adsorption was found at the negative electrode ($X = 1$) and ion exchange at the positive ($X = 0$) [18], confirming results obtained using electrochemical quartz crystal microbalance technique under a gravimetric mode [20]. In addition, the effective ionic diffusion coefficients inside the carbon nanopores were decreased by two orders of magnitude compared with bulk electrolyte [19**]; this was explained by the increase of the ion population in pores. As a result, the charging mechanism (counter ion adsorption versus ion exchange) affects the ion transport kinetics in confined nanopores.

Conventional techniques have been also developed to study ion transfer in porous carbons. Interestingly, *in situ* dilatometry measurement during electrochemical polarization shows also an asymmetric behavior with respect to the electrode polarization, the electrode thickness change being more important during negative polarization [21]. Recently, Presser *et al.* improved the technique by coupling *in situ* dilatometry together with X-ray absorption spectroscopy (XAS) [22**] [21]. First, they confirmed the asymmetric swelling of porous carbon electrodes during

electrochemical polarization in aqueous electrolytes. Also, thanks to the use of porous carbon with hierarchical microporous/mesoporous structure, most of the volume change could be assigned to the presence of pores less than 1 nm size. The origin of the asymmetry was attributed to the increase of the C–C bonds due to electron injection into the carbon during negative polarization. This echoes the increase in the ion population reported by Forse and co-workers by *in situ* NMR spectroscopy [15], leading to the decrease of the ionic diffusion coefficient in carbon nanopores.

Finally, the development of *in situ* X-ray or neutron scattering techniques has been particularly successful for studying ion adsorption in carbon nanopores [23**–25]. Prehal *et al.* [24] used CsCl aqueous electrolyte to study the ion adsorption in nanoporous carbons under polarization. By coupling SAXS and Monte Carlo modeling, they evidenced the ion partial desolvation when confined in carbon nanopores. The extent of desolvation and confinement was found to increase with the applied potential, in agreement with previous studies [26], which gives hints to explain the capacitance increase in carbon nanopores. Also, Futamura *et al.* recently showed the existence of co-ion pairs when the ionic liquid electrolyte was confined into carbon pores of 0.7 nm size, that is when the ion size is close to the pore size [25]. Such an improved co-ion pairing was the consequence of the partial breaking of the electrostatic Coulombic repulsion interactions between co-ions thanks to the creation of image charges in the carbon. They could confirm the creation of a “super ionic” state such as predicted by Kornyshev and Kondrat from modeling [27].

Figure 3



Schematic of the cavity micro-electrode. Adapted with permission from ref. [40].

As one can see, the more we advance in the understanding of the ion confinement effect in nanopores, the more things get complex. There is still a lot to understand in this field and all these analytical tools will be of great help to keep on moving in this direction.

Pseudocapacitive and high charge–discharge rate materials

Pseudocapacitive materials store the charge through fast, non-diffusion-limited redox reactions. Also, different from amorphous porous carbon materials used in EDLCs, most of the pseudocapacitive materials show organized crystalline structure. So, most of the conventional techniques based on X-ray diffraction or scattering used to characterize battery electrode materials have been employed with pseudocapacitive materials. We will then just briefly mention some examples. *In situ* XRD has been extensively used to study the swelling/contraction of pseudocapacitive materials during ion intercalation/de-intercalation, such as in MnO_2 , NiO_x , or MXene [28–30]. Without surprise, the electrode material volume changes are driven by electrostatic repulsion between the layers or the steric effects coming from ion intercalation/de-intercalation to balance the charge [29]. In monocrystalline Nb_2O_5 operating in non-aqueous electrolytes, the intercalation/de-intercalation process volume change is driven by steric effect (swelling during intercalation, contraction during de de-intercalation) [31]. X-ray absorption was used to evidence the change of the Ti oxidation

state during charge/discharge of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrode [32,33], as well as in other materials [34,35].

Differently, micro-electrodes or cavity micro-electrodes tools (Figure 3) are well-suited for the electrochemical characterization of high-rate pseudocapacitive materials. Thanks to the small amount of materials tested, a large range of potential scan rates (v) can be explored—from few mV s^{-1} up to few V s^{-1} —which was extremely useful for studying the electrochemical kinetics of pseudocapacitive reactions [36–38]. The deconvolution of the current into non-diffusion limited surface process (changing with v) and diffusion-limited (changing with $v^{1/2}$) has made it possible to extract the pseudocapacitive contribution to the total current at each potential, which helps in optimizing the structures to design high-rate materials [36–39].

Another original initiative comes from Hu *et al.*, who used Raman spectroscopy to characterize the charge storage during polarization of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrodes in SO_4^{2-} ions containing aqueous electrolyte of various cations [41••]. MXenes are 2-Dimensional materials pioneered by Barsoum and co-workers [42], which contains O- and F- surface terminations. Those groups come from the synthesis process, that is etching of MAX phase in the fluorine-containing acidic solutions [33]. It was found that hydronium ions in sulfuric acid could bond with the oxygen-containing terminations of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene negative electrode upon reduction (oxidation) while debonding occurs upon oxidation (reduction) [41••]. This

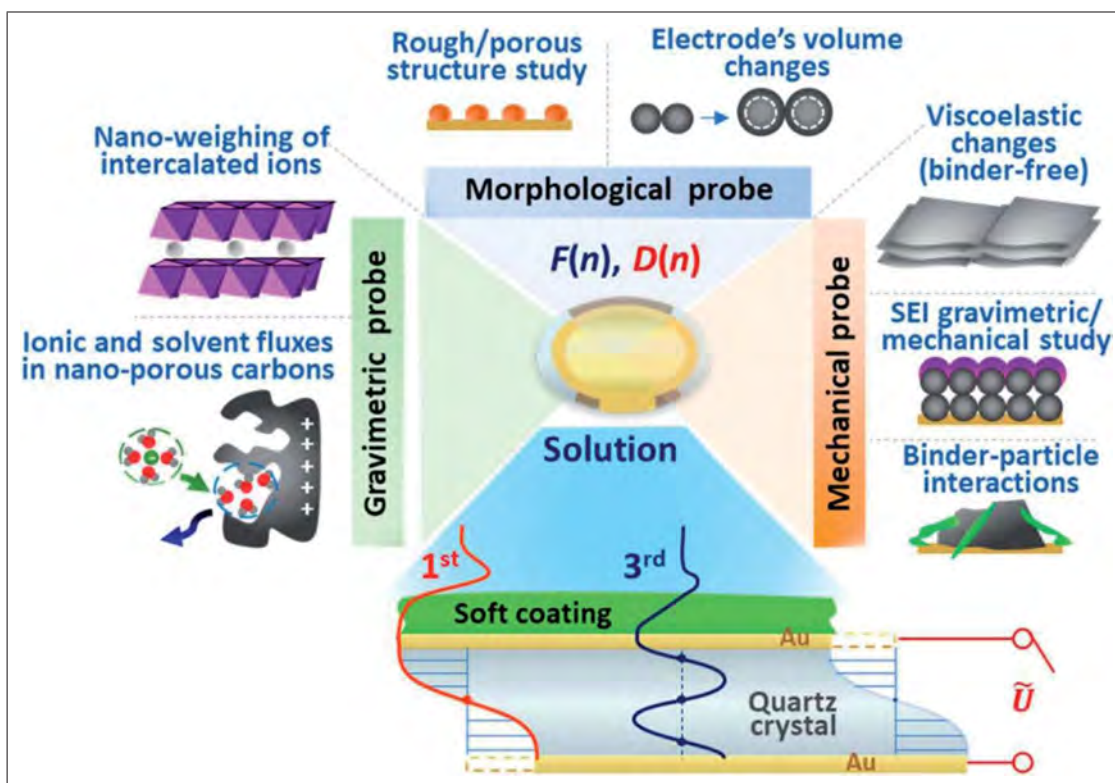
process is accompanied by a change in the oxidation state of Ti from Ti (+III) down to Ti(+II). The redox reaction on Ti explains the extremely high capacitance $\text{Ti}_3\text{C}_2\text{T}_x$ MXene can reach in acidic electrolytes [33,43]. In contrast, in neutral electrolytes, only double layer adsorption occurs without charge transfer on Ti atoms [41**]. Broadening the use of *in situ* Raman spectroscopy technique to other materials could bring new insights in the pseudocapacitive charge storage mechanism.

The discovery of 2D MXene materials has boosted the research in pseudocapacitive materials. One of the key features of MXenes is the presence of surface oxygen and fluorine terminations on their surface. The TPD-MS technique has been successfully used to measure the change of the amount and the nature of these groups during hydrazine intercalation into $\text{Ti}_3\text{C}_2\text{T}_x$ MXene material [44]. The capacitance of MXene in the non-aqueous electrolyte is well behind that in the aqueous acidic electrolytes [45] and the charge storage mechanism of MXenes in non-aqueous electrolytes is still unclear [28,46]. *In situ* dilatometry technique, which is well-suited for 2D materials, has been used to measure the swelling/expansion of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrode in

imidazolium-based ionic liquid electrolyte [47]. MXene electrode swelling was measured during negative polarization, suggesting the preferential insertion of cations. Under positive polarization, the electrode contracts even further compared to the un-polarized sample, suggesting an ion exchange mechanism. Similar results were obtained from *in situ* XRD measurements [28] and a molecular dynamics simulation study [48], which confirm the difference in the charge storage mechanism with the electrode polarity. Also, the modest capacitance suggests a major contribution from the double layer.

New analytical tools based on the electrochemical quartz crystal microbalance (EQCM) technique have also been developed to study energy storage materials that offer interesting opportunities in the EC area. Differently from the gravimetric EQCM, the EQCM with dissipation monitoring (EQCM-D) operated with multiple overtones of the resonance frequency, thus probing a wide range of penetration depth δ_n [49,50]. The structural parameters of the electrodes can be obtained by measuring the change in the resonance frequency ΔF and the change in the full-width at half-height of the resonance peak ΔW over a wide range of overtone numbers n , and fitting the

Figure 4



Gravimetric and non-gravimetric applications of EQCM-D for the characterization of energy-storage electrodes. (Bottom panel) Acoustic waves for fundamental frequency and its 3rd overtone. Adapted with permission from ref. [49]. Copyright© 2018 American Chemical Society.

hydrodynamic equations. Structural parameters include electrode film density or thickness, permeability length, particles radius and coverage density (Figure 4) [49]. This technique is an efficient tool for tracking in one shot the geometrical change in the electrodes (contraction or swelling, morphological changes) as well as the change in reaction mechanisms (formation of passive layers or electrolyte decomposition) [51**].

Another technique derived from EQCM is called AC-electrogravimetry or AC-EQCM [52]. The AC-EQCM technique consists of achieving gravimetric EQCM measurements at a steady state (constant potential for instance) and over-impose a sinusoidal perturbation to the bias signal such as achieved in electrochemical impedance spectroscopy. Differently from gravimetric EQCM, AC-EQCM allows the deconvolution of a global gravimetric EQCM response into individual cations, anions, and solvent molecules contributions by plotting the dQ/dE (Q : charge, E : potential) or dm/dE (m : mass, E : potential) transfer functions; this is one key advantage of this technique which can track the electrochemical activity of one type of anion (cation) in a mixture of anions (cations) [53]. Some papers have just been published describing the use of AC-EQCM to study pseudocapacitive materials [54*]. The possibility for differentiating the ion contributions present great interest for studying the charge storage reaction mechanisms in various electrolytes.

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AC-electrogravimetry (ac-EQCM) was used for the first time for studying pseudocapacitive charge storage mechanism. Results clearly evidence the de-hydration of different cations when transfer to the electrode/electrolyte interfaces. The reaction kinetics and resistance of charged and noncharged species transferred at the electrode/electrolyte interfaces and the number of water molecules in the hydration shell of the ions were estimated as well as the flux of free water.