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Study of Prussian Blue (PB) films by ac-electrogravimetry: influence of PB morphology on ions movement

J.J. García-Jareño [a,b], A. Sanmatías [a], F. Vicente [a], C. Gabrielli [b], M. Keddam [b], H. Perrot [b,*]

[a] *Department Química-Física, Facultad de Química, Universidad de Valencia, C/Dr. Moliner 50, 46100 Burjassot, Spain*
[b] *LPLE, UPR 15 du CNRS, Université Pierre de Marie Curie, Physique des Liquides et Electrochimie, Tour 22, 4 Place Jussieu, 75252 Paris, France*

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Abstract

The electrochemical response of Prussian Blue films in NaCl solutions was studied. It was proved that the stability with cycling of PB films increased when these films are covered with a Nafion® membrane. This fact allows PB films to be studied in NaCl solutions under steady state conditions by impedance spectroscopy and ac-electrogravimetry. A model, which can explain the differences between the electrochemical behaviour of amorphous PB films and crystalline PB films in NaCl solutions, is proposed. This model is based on the hypothesis of a partial dehydration of the sodium ions before the electrochemical reactions take place, allowing the transport of sodium ions through the zeolitic channels of Prussian Blue. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Prussian Blue Films; Nafion®; Sodium countercation; Quartz crystal microbalance

1. Introduction

Prussian Blue (PB) films deposited on the surface of an electrode were first obtained by V.D. Neff [1] in 1978. Their use in electrochromic devices, rechargeable batteries or for electrocatalytic applications described in literature have increased their technological interest. On the other hand, the possibility of obtaining films with an extremely ordered inner structure makes these films one of the most widely studied systems [2–10].

Several papers have suggested the possibility of different electrochemical behaviours depending on the degree of order in the structure of the films [2,11]. The order in the structure has proved to be dependent on the electrogeneration conditions. More amorphous PB films are obtained by applying larger currents during the electrodeposition reaction (a-PB films), while for lower electrodeposition currents more crystalline PB films (c-PB films) are obtained.

Prussian Blue films in their insoluble structure, as they are deposited according to Itaya et al. [2–4], can be reduced to the colourless compound Everitt's Salt (ES) by means of the following reaction [2]:

$$\underset{\text{Prussian Blue}}{Fe_4^{III}\ [Fe^{II}(CN)_6]_3} + 4K^+ + 4e^- \rightleftarrows \underset{\text{Everitts Salt}}{K_4Fe_4^{II}[Fe^{II}(CN)_6]_3} \quad \text{(i)}$$

and oxidized to the Prussian Yellow (PY) form in solutions containing Cl^- anions by:

* Corresponding author. Tel.: +33-1-4427-7216; fax: +33-1-4427-4074.
E-mail address: perrot@ccr.jussieu.fr (H. Perrot).

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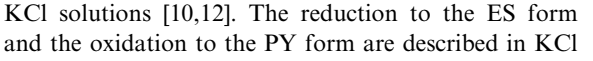

$$Fe_4^{III}[Fe^{II}(CN)_6]_3 + 3Cl^- \rightleftarrows Fe_4^{III}[Fe^{III}(CN)_6]_3Cl_3 + 3e^- \quad \text{(ii)}$$

insoluble PB insoluble PY

Anyway, it is known that insoluble PB films are converted to a soluble structure of the films by successive cycling around the reduction system PB⇔ES in KCl solutions [10,12]. The reduction to the ES form and the oxidation to the PY form are described in KCl solutions for the soluble PB structure by [2]:

$$KFe^{III}Fe^{II}(CN)_6 + K^+ + e^- \rightleftarrows K_2Fe^{II}Fe^{II}(CN)_6 \quad \text{(iii)}$$

soluble PB soluble ES

for the reduction process and:

$$KFe^{III}Fe^{II}(CN)_6 + Cl^- \rightleftarrows KFe^{III}Fe^{III}(CN)_6Cl + e^- \quad \text{(iv)}$$

soluble PB soluble PY

for the oxidation process. It should be noted that the name of 'soluble PB' is related to the incorporation of potassium ions inside the insoluble PB after several potential cycling.

According to reactions i and iii, during the electrochemical reduction of PB films to the ES form, some countercations should enter the film in order to maintain electroneutrality. As the structure of PB films has been described as a zeolitic building with channels of 3.2 Å in diameter [13,14], only a few counterions with hydrated radius smaller than the size of the pore of the PB films can be transported through the PB structure. That way, only voltammetric studies of PB films in solutions containing K^+, NH_4^+, Cs^+ and Rb^+ ions showed good results of stability during the repetitive voltammetric cycles around the PB⇔ES process [2,15]. The diameter of the Na^+ hydrated ion is about 3.66 Å, which is slightly larger than the size of the pore in the PB structure. Therefore, electrochemical studies of PB films in NaCl solutions have shown poor stability results [2]. However, it has been proved that this reduction process takes place [2] when more amorphous PB films are studied. This electrochemical behaviour has been explained by assuming that the sodium ion can move through the amorphous Prussian Blue films as the size of their inner pores is larger than for more crystalline films.

Nevertheless, these results are not clarified yet considering that the electric charge measured from the voltammetric peak of an amorphous PB film in a NaCl solution is very close to the electrodeposition charge. This fact implies that the whole PB film be electroactive, and therefore it must be necessary that sodium ions move inside the zeolitic channels of PB films during the redox processes, which is not possible since the diameter of the hydrated sodium ion is larger than the size of the zeolitic channel.

The possibility of covering the PB film by a Nafion® layer was shown to be of special interest in the development of electrochromic devices [16,17], but also, in electrocatalytic applications by fixing the catalyst on the PB films by covering the electrode with the Nafion® membrane [18]. However, the presence of Nafion® layers also modifies the electrochemical response of PB films in KCl solutions as has been shown in a recent study [19]. This membrane represents an additional resistance to ion transport, but also the dehydration process of the Nafion® membrane, in contact with the KCl solution, causes the dehydration of the inner PB film.

It has been proved that the degree of hydration of the PB films plays an important role during these electrochemical processes [7,20–23]. Therefore, the number of hydration of counterions should be a very important factor to be considered in the analysis of experimental results.

From voltammetric or electrochemical impedance results it is not possible to obtain information on the number of hydration of the ions that are inserted or expelled from the film during electrochemical experiments. Therefore, it is necessary to obtain other data by another experimental technique which permits the measurement of mass changes inside the film associated with the electrochemical processes in addition to the measured electrical current. This information can be provided by quartz crystal microbalance (QCM) measurements.

Moreover, to get a better analysis of the various processes the QCM was also used under alternative regime: ac electrogravimetry allows the mass response to a small potential perturbation to be analysed thanks to a fast quartz crystal microbalance used in dynamic regime [24–30]. This technique has been already used for other polymers [24,30–33] and oxides ib28" > [28] where attractive informations were collected for clarifying the species movement involved in the various reactions.

2. Theory

The motion of counterions through the film accompanies the transport of electrons to maintain the electroneutrality of the film. In some polymers it is the counterion transport which is the rate controlling step of charge transport. In other polymers, the rate of charge transport is controlled by the slow transport of electron through the film. In both cases, the expressions that represent the rate of charge transport through the electroactive films are mathematically identical and whichever the species which move through the electroactive film, the process can be characterised by means of an apparent coefficient of diffusion of electrons or counterions [34–36].

Fig. 1 shows the scheme of the electrode/PB film/solution. Since PB films are studied in acidic NaCl solutions, both hydronium and sodium ions, c_1 and c_2, chloride anion, a, and water, s, can eventually move through the film during the charge transport process.

The geometry of the modified electrode is shown in Fig. 1. By definition, the fluxes of species i, J_i, are positive for outgoing ions:

$$J_i > 0 \quad \text{for} \quad x > 0 \tag{1}$$

The charge transfer mechanism, which occurs at the film/electrolyte interface during an oxidation or reduction reaction of the film in aqueous media, can be modelled by assuming that the transport of the species in the electrolyte is sufficiently fast and is not a limiting step.

2.1. Boundary conditions

The following boundary conditions are supposed to be applied at the electrode/film interface as anions, cations and solvent cannot cross the interface:

$$\text{At } x = 0 \quad J_a(0) = J_{c1}(0) = J_{c2}(0) = J_S(0) = 0 \tag{2}$$

On the other hand, as outwards positive fluxes give negative currents for expelled cations, by assuming monovalent ions at the polymer/electrolyte interface:

$$\text{At } x = d \quad -J_a(d) + J_{c1}(d) + J_{c2}(d) = \frac{I_F}{F} \tag{3}$$

where I_F is the Faradaic current density, d is the thickness of the film and F the Faraday number.

The generalized insertion rates, according to classical heterogeneous kinetic laws, for the species i are supposed to be such as:

$$J_i(\mathrm{d}) = k_i(C_i - C_{i_{\min}}) - k'_i(C_{i_{\max}} - C_i)C_i^0 \quad i = \mathrm{a,\ c} \tag{4}$$

where $C_{i_{\max}}$, is the maximum concentration of sites available for ion insertion, $C_{i_{\min}}$ is the minimum concentration of sites occupied by ions i in the host material and C_i^0 is the concentration of species i in the solution.

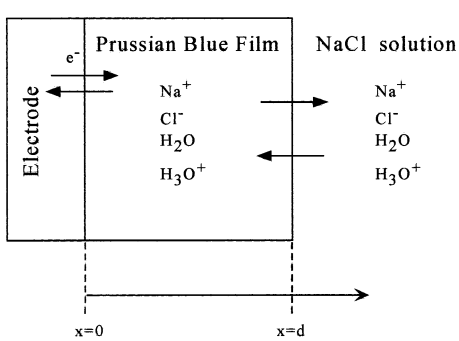

Fig. 1. Scheme of the electrode/PB film/NaCl solution.

2.2. Steady-state and quasi steady-state

At steady-state, it was shown that [37,38]:

$$\frac{\mathrm{d}C_i(E)}{\mathrm{d}E} = \frac{b_i - b'_i}{4} \frac{C_{i_{\max}} - C_{i_{\min}}}{\cosh^2\left[\frac{(b'_i - b_i)(E - E_i^0 - E_i)}{2}\right]} \tag{5}$$

and has a maximum for $E = E_i^0 + E_i$ equal to:

$$\left(\frac{\mathrm{d}C}{\mathrm{d}E}\right)_{\max} = \frac{(C_{i_{\max}} - C_{i_{\min}})}{4}(b'_i - b_i) \tag{6}$$

where E_i is such as:

$$C_i^0 \frac{k'_{i0}}{k_{i0}} = \exp[-(b'_i - b_i)E_i] \tag{7}$$

2.3. Dynamic behaviour

In dynamic regime, by linearizing the equations which govern the process and using the boundary conditions, it can be shown that [37,38]

$$\frac{\Delta J_i(d)}{\Delta E} = \frac{G_i}{1 + K_i \frac{\coth\left(d\sqrt{\frac{j\omega}{D_i}}\right)}{\sqrt{j\omega D_i}}} \quad i = a,\ c,\ s \tag{8}$$

where G_i and K_i can be calculated from Eq. (4), d is the film thickness and D_i the diffusion coefficient of the species i.

Considering the behaviour in the frequency domain, the electrochemical impedance, $Z_F(\omega)$, and the electrogravimetric transfer function $(\Delta m/\Delta E)(\omega)$, are obtained:

$$Z_F^{-1}(\omega) = \mathrm{F}\left(-\frac{\Delta J_a(d)}{\Delta E} + \frac{\Delta J_{c1}(d)}{\Delta E} + \frac{\Delta J_{c2}(d)}{\Delta E}\right) \tag{9}$$

$$\frac{\Delta m}{\Delta E}(\omega) = \frac{-A}{j\omega}\left[m_a\frac{\Delta J_a}{\Delta E} + m_{c1}\frac{\Delta J_{c1}}{\Delta E} + m_{c2}\frac{\Delta J_{c2}}{\Delta E} + m_s\frac{\Delta J_s}{\Delta E}\right] \tag{10}$$

where m_a, m_{c1}, m_{c2}, and m_s are the atomic masses of anions, cations and solvent (the mass of the electron is supposed to be zero). Obviously, the charged species, anions and cations, are involved in $Z_F(\omega)$, whereas $(\Delta m/\Delta E)(\omega)$depends on anions, cations and solvent all together.

Another quantity, $(\Delta m/\Delta q)(\omega)$, such as

$$\frac{\Delta m}{\Delta q}(\omega) = j\omega Z_F \frac{\Delta m}{\Delta E}(\omega) \tag{11}$$

can provide information on the mass of the species which is inserted or expelled at each frequency.

2.4. Diagnostic criteria

From Eqs. (9) and (10), it is possible to eliminate the contribution of Cl^- anions from the $\Delta m/\Delta E$ function by considering:

$$\frac{\Delta m_{-\mathrm{Cl}^-}}{\Delta E} = \frac{\Delta m}{\Delta E} - \frac{m_{\mathrm{Cl}^-}}{j\omega}\frac{1}{FZ_{\mathrm{F}}} \tag{12}$$

which takes into account only the contribution of cations and solvent. This operation was performed in order to check the efficiency of the Nafion layer: indeed, if this latter play the role of blocking barrier for chloride ion, the previous calculated partial mass/potential transfer function will be equal to the experimental and initial $\Delta m/\Delta E$.

This partial electrogravimetric transfer function is equal to:

$$\frac{\Delta m_{-\mathrm{Cl}^-}}{\Delta E}(\omega) = -\frac{1}{j\omega}\left[(m_{\mathrm{Cl}^-}+m_{\mathrm{Na}^+})\frac{\Delta J_{\mathrm{Na}^+}(d)}{\Delta E} + (m_{\mathrm{Cl}^-}+m_{\mathrm{H_3O}^+})\frac{\Delta J_{\mathrm{H_3O}^+}(d)}{\Delta E} + m_{\mathrm{H_2O}}\frac{\Delta J_{\mathrm{H_2O}}(d)}{\Delta E}\right] \tag{13}$$

It should be noted that the Na^+ and H_3O^+ contributions calculated above are emphasised as their respective $\Delta J_i/\Delta E$ terms are multiplied by an increased mass, respectively, $m_{\mathrm{Cl}^-}+m_{\mathrm{Na}^+}$ and $m_{\mathrm{Cl}^-}+m_{\mathrm{H_3O}^+}$ if compared with the original Eq. (10).

In the same way, if the sodium contribution is eliminated in the mass change function, the partial electrogravimetric transfer functions resulting is:

$$\frac{\Delta m_{-\mathrm{Na}^+}}{\Delta E} = \frac{\Delta m}{\Delta E} + \frac{m_{\mathrm{Na}^+}}{j\omega}\frac{1}{FZ_{\mathrm{F}}} \tag{14}$$

$$\frac{\Delta m_{-\mathrm{Na}^+}}{\Delta E}(\omega) = -\frac{1}{j\omega}\left[(m_{\mathrm{Cl}^-}+m_{\mathrm{Na}^+})\frac{\Delta J_{\mathrm{Cl}^-}(d)}{\Delta E} + (m_{\mathrm{H_3O}^+}-m_{\mathrm{Na}^+})\frac{\Delta J_{\mathrm{H_3O}^+}(d)}{\Delta E} + m_{\mathrm{H_2O}}\frac{\Delta J_{\mathrm{H_2O}}(d)}{\Delta E}\right] \tag{15}$$

From the plot of the partial electrogravimetric transfer functions the number of species involved in the charge compensation process can be evaluated without any doubt.

3. Experimental

The changes of the resonance frequency of the quartz crystal, Δf can be related to changes of the mass of the film deposited on the gold electrode, Δm, by means of the Sauerbrey equation [39]:

$$\Delta f = -\frac{2f_0^2}{\sqrt{\rho_{\mathrm{Q}}\mu_{\mathrm{Q}}}}\frac{\Delta m}{A} \tag{16}$$

where ρ_{Q} is the quartz density (2.648 g/cm^3), μ_{Q} is the quartz shear modulus (2.947×10^{11} dynes/cm^2), f_0 is the unloaded quartz crystal resonance frequency and A is the piezoelectrically active area. The conditions of applicability of this equation imply that the film deposited onto the gold electrode is sufficiently rigid. Unfortunately, this condition was not valid for our PB film, which exhibited a pronounced viscoelastic behaviour according to electroacoustic admittance analysis. But with very thin PB layers, $d = 0.14$ μm, this viscoelastic behaviour does not affect drastically the mass sensitivity coefficient and moreover remained constant when the potential was changed [40].

Therefore, if PB films were grown on one of the gold electrode of the quartz crystal it is possible to simultaneously obtain the voltammetric curve (current vs. potential) and the mass change against the cycled potential.

On the other hand, a sinusoidal signal with a small amplitude perturbation was applied to the electrode at a fixed potential after stabilisation where a zero current was reached. From the analysis of the response of the electrode in a large frequency range the impedance,$(\Delta E/\Delta I)(\omega)$, and the electrogravimetric transfert function $(\Delta m/\Delta E)(\omega)$ were simultaneously obtained.

PB films were galvanostatically deposited on ITO (Indian Tin Oxide) electrodes ($A_{\mathrm{geom}} = 1$ cm^2, GLASSTRON) [2] for classical voltammetric curves. $FeCl_3$ (chemically pure), $K_3Fe(CN)_6$, KCl, NaCl and HCl (p.a.) (A.R. PANREAC) were used for the synthesis of PB films. Water was distilled and deionised (Milli Q-plus-MILLIPORE). ITO electrodes were immersed into $K_3(Fe(CN)_6)$ 0.02 M, $FeCl_3$ 0.02 M and HCl 0.01 M solution and a controlled cathodic current of $i_c = 40$ μA/cm^2 was applied for 150s for c-PB electrodeposition. When this current was increased to 600 μA/cm^2, a-PB films were obtained. For gravimetric measurements, PB was deposited onto gold electrodes following the same procedure.

The Nafion® (perfluorinated ion-exchange membrane) 5 wt.% stock solution in low aliphatic alcohols and 10% water was supplied by Aldrich (Ref. 27,470-4). Nafion® films were deposited on the PB film by extending the appropriate volume of Nafion® solution and allowing the solvent to evaporate at room temperature: 25 μl for the ITO/PB electrode (A = 1 cm^2) and 4 μl of a 2:5 diluted Nafion®: aliphatic alcohols solution on the gold/PB system ($A = 0.25$ cm^2). The thickness of the Nafion® film was calculated from the electrode surface area assuming a dry Nafion® density of 1.98 g/cm^3 and an about 1 g/cm^3 solution density (about 6 μm for ITO/PB electrodes and 1.5 μm for gold/PB electrodes).

Electrochemical experiments were carried out by means of a typical three electrodes cell where the PB/

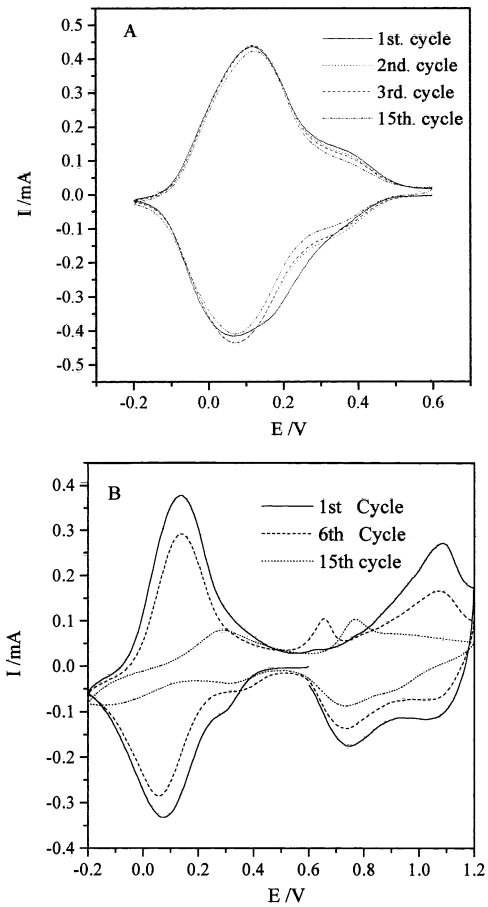

Fig. 2. Voltammograms of an 'insoluble' c-PB film covered by a Nafion® layer (6 μm thickness) in a NaCl 1 M solution and acid pH 3.0. Voltammograms are carried out at 0.02 V/s, (A) from 0.6 to −0.2 V against the reference electrode Ag/AgCl/NaCl (1 M) and (B) from 0.6 to −0.2 V and the reverse sweep from −0.2 to 1.2 V against the reference electrode Ag/AgCl/NaCl (1 M).

Nafion® films deposited on the ITO glass or gold were used as the working electrode, a platinum plate (4 cm^2) was the counter electrode and Ag/AgCl/KCl (1 M) or Ag/AgCl/NaCl (1 M) and SCE were used as reference electrodes in various measurements. A four-channel frequency response analyser SOLARTRON 1254 and SOTELEM P.G.STAT.Z.1 potentiostat were used for the studies. Electrochemical experiments were carried out in 1 M and 0.5 M NaCl [2–9].

The impedance and electrogravimetric response were measured in the 0.01 Hz to 10^5 Hz frequency range and 10 mV of signal amplitude. The fitting of experimental impedance and electrogravimetric data to the theoretical expression was carried out by means of a non-linear least squares procedure based on the Marquardt algorithm for function optimisation [41].

4. Results

4.1. Crystalline PB film

4.1.1. Cyclic voltammetry

The presence of a Nafion® layer covering the PB films modifies their electrochemical properties [19]. Fig. 2A shows the voltammograms of an ITO/insoluble (potassium-free) c-PB (crystalline) film covered by a 6-μm thick Nafion® membrane in a 1-M NaCl aqueous solution and acid pH (pH 2.2). It can be observed that after 15 cycles the voltammetric wave shape was still well defined, and furthermore, the electric charge enclosed in the voltammetric peak (6.1×10^{-3} C) was in agreement with the electrodeposition charge (6 mC). These PB films were generated at a 40 $\mu A/cm^2$ current deposition, which corresponds to an ordered structure (c-PB films). When they were not covered by Nafion® layers their voltammetric response in NaCl solutions had a very poor stability [2]. When these PB/Nafion® films were studied along the whole voltammogram, PY⇔PB⇔ES, the film degradated quickly and the electrochemical response disappeared in a few cycles as shown in Fig. 2B. This behaviour is typical for the insoluble PB films as it has been proved in previous studies of stability of PB films for the successive cyclings [42,43]. In fact, the voltammetric response of insoluble PB films covered by Nafion® layers around the PB⇔ES process in KCl solutions shown that the transformation to the soluble PB structure did not take place [19]. Here, in NaCl solutions a similar behaviour was obtained, and during the first cycles around the PB⇔ES process, as shown in Fig. 2A, the shape of the peaks did not vary, and the transformation to the soluble PB structure did not occur. This means that this poor stability of PB films should be attributed to the fact that the PB films were in the insoluble form.

The study of the electrochemical response of soluble (with inner potassium) c-PB films covered by Nafion® layers in NaCl solutions were also attractive. Soluble PB films were obtained by cycling 15 times insoluble PB films around the reduction system peaks PB⇔ES in a 1-M KCl solution before the PB films were covered by the Nafion® layers. Fig. 3A shows the voltammetric curves obtained for these films in a 1-M NaCl solution: no difference appeared between the successive cycles. Furthermore, the stability of the voltammogram (PY⇔PB⇔ES) was also strongly increased as shown in Fig. 3B, if compared with Fig. 2B.

It is important to note that a well defined system of peaks appeared corresponding to the PB⇔PY process,

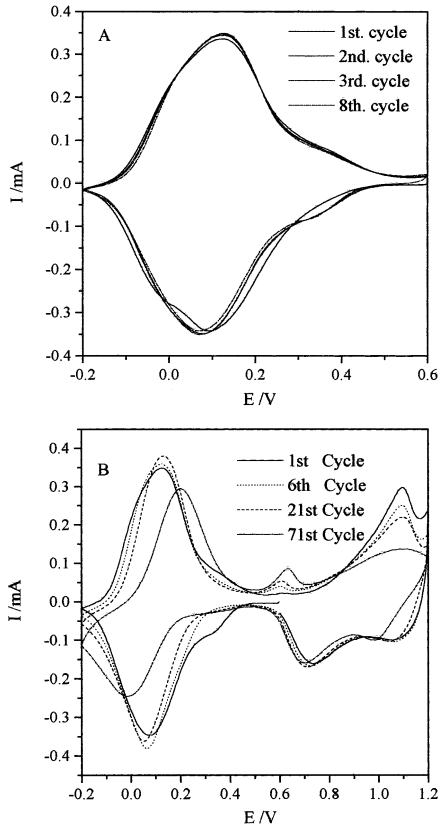

Fig. 3. Voltammograms for a 'soluble' (previously cycled in a KCl solution) c-PB film covered by a Nafion® layer (6 μm thickness) in a NaCl 1 M solution and acid pH 3.0. Voltammograms are carried out at 0.02 V/s, (A) from 0.6 to −0.2 against the reference electrode Ag/AgCl/NaCl (1 M) and (B) from −0.2 to 1.2 V against reference electrode Ag/AgCl/NaCl (1 M).

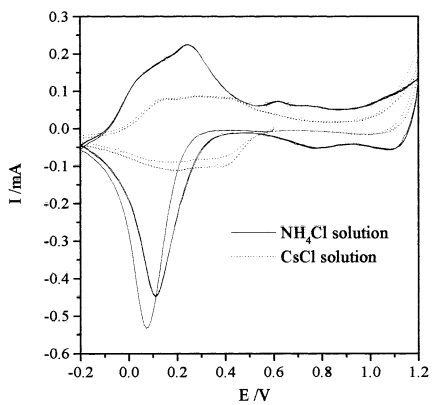

Fig. 4. Whole voltammograms of c-PB films covered by a Nafion® layer (6 μm thickness) in CsCl and NH_4Cl 0.5 M solutions and acid pH (between 2.5 and 2.7). Voltammograms are carried out at 0.02 V from 0.6 to −0.2 V and the reverse sweep from −0.2 to 1.2 V against the reference electrode Ag/AgCl/NaCl (1 M).

and the colour change from blue to yellow can be observed. The system of peaks can only be clearly observed in KCl and NaCl solutions, while for PB films in NH_4Cl or CsCl solutions this system of peaks is poorly observed [15]. This system of peaks was either observed when the films of Prussian Blue were covered with Nafion® in CsCl and NH_4Cl solution (Fig. 4).

Some features were not clear. The first one was the fact that during the oxidation process, according to reactions ii and iv, Cl^- anions should enter the PB film to maintain electroneutrality. However, it is known that the transport of anions is almost entirely suppressed through the Nafion® membrane [44]. This perm-selectivity of Nafion® membranes implies that the oxidation process to the yellow form cannot take place according to reactions ii and iv. Some authors have pointed up the possibility that the compensation of the electric charge within the film occurs by the exit of countercations instead of the entrance of the anions during the oxidation process [5,9,45]. This idea is supported by several experimental results such as the independence of the formal potential for this system of peaks on the nature of the counteranion [42] or the dependence of this potential on the potassium concentration [9,12,45]. Also, impedance studies of PB films in NH_4Cl, CsCl and KCl solutions at potentials corresponding to the PB⇔PY process, have shown that the countercations should play an important role during the oxidation process [15]. This is supported by the fact that the potential at which the resistance of charge transport through the film [6,7], reach minimum values is different in the three studied solutions.

Another questionable point is the fact that although the Na^+ hydrated ions cannot be transported through the PB films, the electrochemical processes which need the entrance of countercations into the film can, nevertheless take place when c-PB films are covered by Nafion® layers or that their structure is more amorphous [2]. In the case of c-PB films covered by Nafion® layers, a very simple explanation is to consider that sodium ions can lose a part of their hydration sphere during the transport through the Nafion®. So, the effective radius or size of the ion decreases and as the size of the pore is only slightly smaller than the size of the hydrated ion, a small decrease in the effective size of the latter allows this ion to be transported through the film.

4.1.2. Cyclic EQCM

To confirm this hypothesis, 'soluble' c-PB films deposited on the gold electrode of a quartz crystal were studied by cyclic voltammetry and QCM investigation. Fig. 5 shows the variation of current and mass against the applied potential. During the reduction process the charge compensation takes place by the incorporation

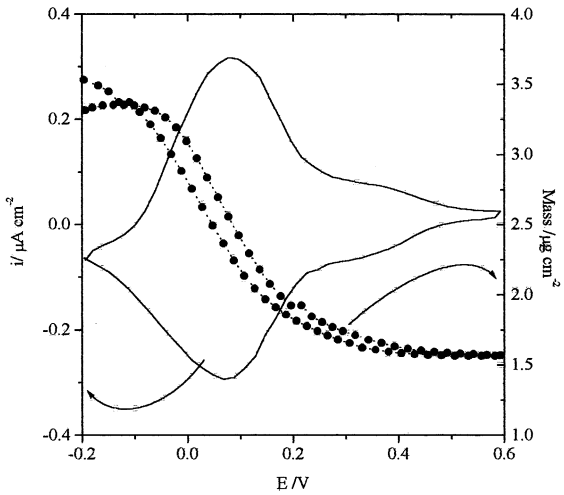

Fig. 5. Curves current versus potential and mass versus potential of a c-PB film covered by a Nafion® layer (1.5 μm) in a 0.5-M NaCl solution, and acid pH. Scan rate = 0.01 V/s, from 0.6 to −0.2 V against the SCE reference electrode.

of sodium cations within the PB film, and no participation of Cl^- anions is expected since PB films are covered by Nafion®. It is possible to partly evaluate the mass of the cation that enters the PB film by the following relationship:

$$m_c = \frac{F\,\Delta m}{Q} \tag{17}$$

where F is the Faraday (96 500 C/mol), Q the electric charge enclosed within the voltammogram (C/cm^2) and Δm the change of mass associated to the reduction of the PB form to the ES form (g/cm^2). The electric charge measured is 0.0086 C/cm^2 and $\Delta m = 2$ μg/cm^2 and then, the mass of the cation which enters the PB film is 22.4 g/mol. By comparing this value with the sodium atomic mass, 23 g/mol, it is concluded that sodium cations are not hydrated when they are inserted within the PB film. To confirm this result, ac electrogravimetry was performed with the same sample. Indeed, this atomic mass value obtained can be questionable because the calculation (Eq. (17)) was used for a QCM measurement on a whole cycle: this QCM response appears as a global mass response taking into account all the motion of the species. On the contrary, ac electrogravimetry can separate the various species motions as the perturbation frequency changes allows the various kinetic processes to be reached.

4.1.3. ac electrogravimetry

Fig. 6 shows the global, $\Delta m/\Delta E$, and partial ac-electrogravimetric transfer functions obtained from Eqs. (12)–(15) for a c-PB film covered with a Nafion® layer in a NaCl solution at 0.1 and 0.05 V potentials. It is observed that when the contribution of sodium ions is eliminated, the residual function, which includes the contributions of solvent, hydrated proton and anions is almost zero for these potentials. So, the $\Delta m/\Delta E$ loop can be attributed, without doubt, to the Na^+ movement and the sign of the $\Delta m/\Delta E$ low frequency limit corroborates the shape of the mass/potential curve. Indeed, a negative real value was obtained for this limit (Fig. 6) which indicates that when the potential decreases the Na^+ ions are inserted inside the film. This is a result coherent with the mass increase observed during the PB reduction (Fig. 5) in steady state experiments.

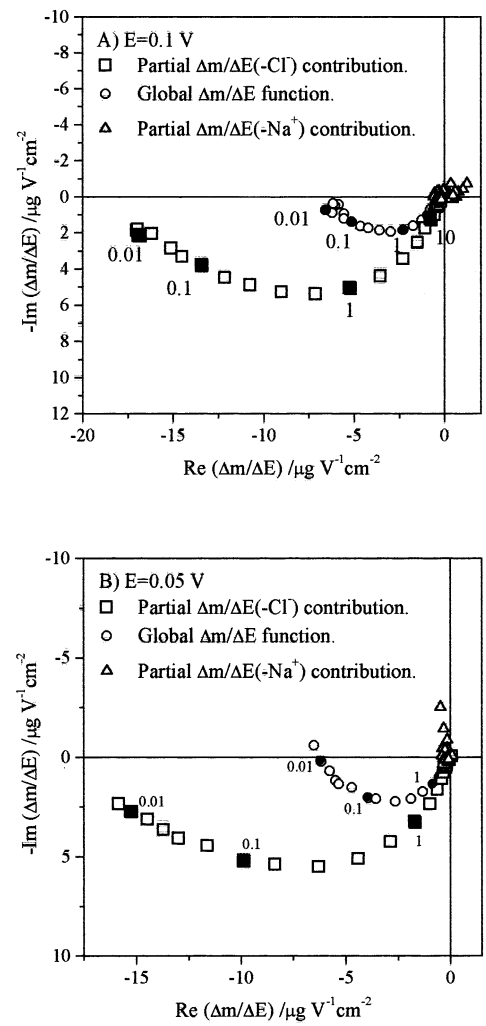

Fig. 6. Global and partial electrogravimetric transfer functions ($\Delta m_i/\Delta E$) for a c-PB film covered by a Nafion® layer (1.5 μm) in a 0.5-M NaCl solution, and acid pH. Potential, $E = 0.1$ V (A) and $E = 0.05$ V (B). Reference electrode SCE. Perturbation signal amplitude $\Delta E = 0.02$ V.

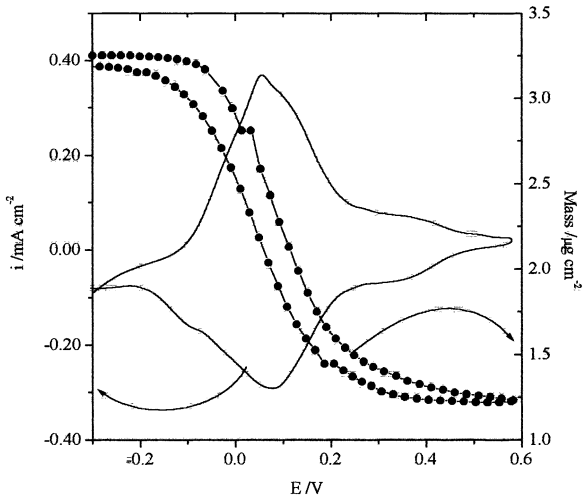

Fig. 7. Curves current versus potential and mass versus potential of an a-PB film in a 0.5-M NaCl solution, and acid pH. Scan rate = 0.01 V/s, from 0.6 to −0.2 V against the SCE reference electrode.

When PB/Nafion® films are studied in NaCl solutions by means of simultaneous impedance spectroscopy and ac-electrogravimetry at various potentials it is also possible to obtain information on the cation mass which enters the PB film at these potentials. From the Faradaic impedance and the electrogravimetric transfer function, the $\Delta m/\Delta q$ function is obtained (Eq. (11)). This function provides information on the mass of the cation that enters the film. If this function is multiplied by the Faraday (96 500 C/mol) the mass of the ion which participates in the charge compensation process is directly obtained. The real part of this function reaches values of 22 g/mol at $E = 0.1$ V and 25 g/mol at $E = 0.05$ V.

4.2. Amorphous PB film

4.2.1. Voltammetry and EQCM measurements

To confirm this dehydration process, amorphous PB films (a-PB films) deposited onto the gold electrode of a quartz crystal were studied by cyclic voltammetry and gravimetry. Fig. 7 shows the current and mass changes against the applied potential. Following the same procedure as for the c-PB/Nafion® system, it is possible to estimate the mass of the cation, which enters the a-PB film during the reduction process. In this case, the electric charge enclosed within the voltammetric curve is $Q = 0.0083$ C/cm^2 and the change in mass associated to this process is $\Delta m = 2.02$ μg/cm^2. Therefore, the estimated mass of the countercation is 23.4 g/mol which corresponds to the non-hydrated sodium cation mass (23 g/mol).

4.2.2. ac electrogravimetry

When a-PB films are studied by electrogravimetry at various potentials between the totally reduced form, Everitt's salt, and the mixed valence compound, Prussian blue, similar conclusions can be drawn. Fig. 8 shows the global and partial electrogravimetric transfer functions at 0.1 and 0.05 V (near the redox potential of the PB⇔ES reaction). In both cases, the partial contribution that corresponds to the elimination of non-hydrated sodium contribution is negligible. Besides, the $F(\Delta m/\Delta q)$ function reaches values near 23 g/mol for the lowest frequencies at these potentials which clearly prove that sodium cations enter the PB film without water whatever the PB film structure.

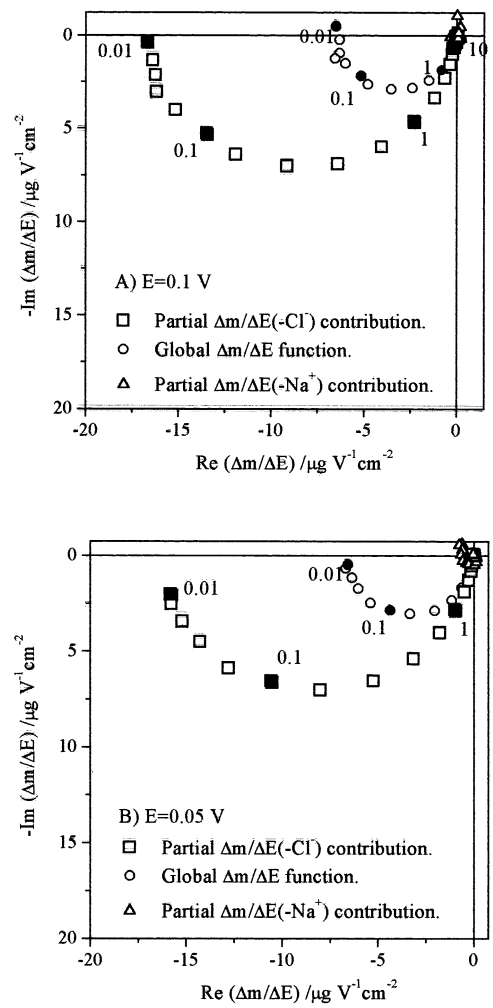

Fig. 8. Global and partial electrogravimetric transfer functions ($\Delta m_i/\Delta E$) for an a-PB film in a 0.5-M NaCl solution, and acid pH. Potential, $E = 0.1$ V (A) and $E = 0.05$ V (B). Reference electrode SCE. Perturbation signal amplitude $\Delta E = 0.02$ V.

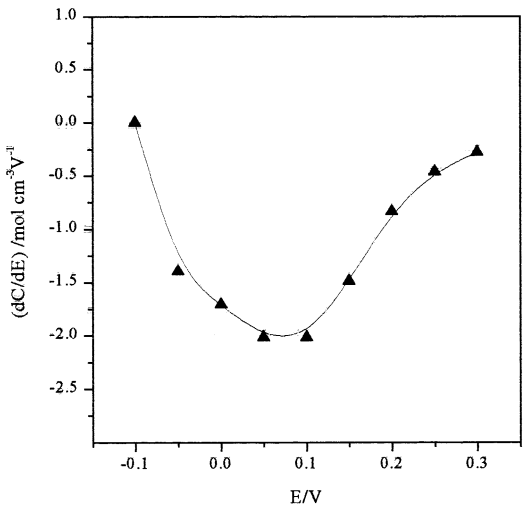

Fig. 9. Derivative of insertion rate for Na^+ ions in amorphous PB films. These values are evaluated from the electrogravimetric curves by extrapolating at lower frequencies.

5. Discussion

In both cases, PB films (a-PB/Nafion® and c-PB/Nafion®) in NaCl solutions show a good electrochemical response and it is corroborated that sodium cations lose their hydration sphere before insertion into the film. Therefore this process takes place at the film/solution interface. The modification of the surface of the PB film allows the dehydration of the cation.

In the case of c-PB films in KCl solutions, it has been also proposed that K^+ ions enter the PB film without water [46]. The energy needed to dehydrate the cation is smaller for the K^+ cation than for the Na^+ cation and also, the number of hydration of Na^+ is larger than the number of hydration of K^+ in the solution. Na^+ cations can enter the a-PB film and not the c-PB film because the more amorphous surface allows the adsorption of sodium cations before the entrance in the film and then catalyse the dehydration process. This process can be expressed as:

$$(Na^+\cdot x(H_2O))_{solution} \rightleftarrows (Na^+\cdot x(H_2O))_{adsorbed} \rightleftarrows (Na^+)_{inserted} + x(H_2O)_{solution}(A)(B)(C) \quad \text{(v)}$$

where x represents the number of water molecules that hydrate the Na^+ cation in the solution.

For Nafion®/PB films it is also concluded that sodium cations enter the PB film without water molecules. That means that the dehydration process takes place at the Nafion®/solution interface. However, it has been reported that sodium cation is transported through Nafion® membranes with water molecules [47,48]. In this case it is also possible to consider that the Nafion® membrane cannot accept more water molecules, and even if the dehydration process takes place at the PB/Nafion® interface, water molecules will be expelled to the outer solution. Therefore, Nafion® in contact with a salt solution loses water since there is an equilibrium between the outer solution and the solution within the Nafion® membrane.

In this case, it is possible to consider that only sodium cations participate to the charge compensation process. Then, from the low frequency limits of the electrogravimetric transfer functions it was possible to obtain the values of the derivative of the insertion isotherms dC/dE (Eq. (15)) for the sodium ion at different potentials which are plotted in Fig. 9 for the a-PB film. dC/dE was calculated from the low frequency limit of $\Delta m/\Delta E$by the following equation:

$$\frac{dC(E)}{dE} = \frac{1}{d \times m_{Na+}} \text{limit}\left(\frac{\Delta m}{\Delta E}\right)_{\omega \to 0} \quad (18)$$

If compared with Fig. 7, a good correlation, about the shape, is observed between the voltammogram and the derivative of the insertion isotherm curve. The minimum in Fig. 9 corresponds to the peak potential in Fig. 7. According to Eq. (6) this potential (0.08 V), which is equal to $E_i^0 + E_i$, represents the redox potential of the PB⇔ES process in NaCl solutions.

If only one charged species participate in the charge compensation process, from Eqs. (8) and (9) the faradaic impedance can be written such as:

$$Z_F^{-1}(\omega) = F\frac{\Delta J_{Na+}}{\Delta E} = F\frac{G_{Na+}}{1 + \frac{K_{Na+}}{d}\frac{\coth\left(\sqrt{j\omega\frac{d^2}{D_{Na+}}}\right)}{\sqrt{j\omega\frac{D_{Na+}}{d^2}}}} \quad (19)$$

According to these results, no important transport of water molecules, associated to the sodium insertion/expulsion process, is observed. Therefore, the electrogravimetric transfer function can be written, according to Eqs. (8) and (10), such as:

$$\frac{\Delta m}{\Delta E}(\omega) = -\frac{A}{j\omega}\left[m_{Na+}\frac{\Delta J_{Na+}}{\Delta E}\right] = -\frac{A}{j\omega}\frac{m_{Na+}G_{Na+}}{1 + \frac{K_{Na+}}{d}\frac{\coth\left(\sqrt{j\omega\frac{d^2}{D_{Na+}}}\right)}{\sqrt{j\omega\frac{D_{Na+}}{d^2}}}} \quad (20)$$

A good way to test the validity of the model proposed here is to fit experimental data of impedance spectra to Eq. (19) and the experimental electrogravimetric data to Eq. (20) and to compare the results obtained. Figs. 10 and 11 show the good correlation

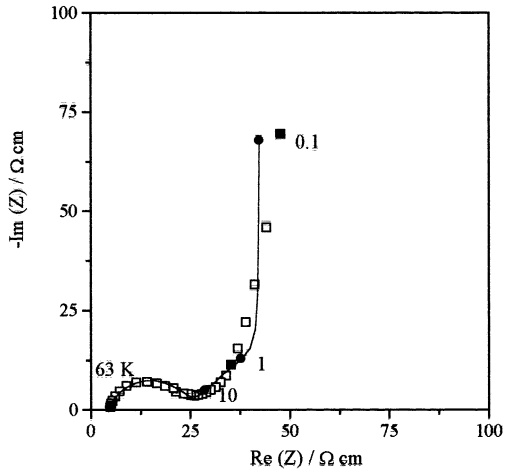

Fig. 10. Experimental impedance spectra (□) and simulated-fitted impedance spectra (—●—). $E = 0.05$ V and amorphous PB film.

between fitted-simulated data and the experimental data for the impedance spectra and the electrogravimetric transfer function.

Table 1 shows the values of the parameters obtained from the fitting of impedance spectra to Eq. (19) and electrogravimetric data to Eq. (20). It is shown that the parameters evaluated from both techniques agree very well, especially in the range of 0.2–0 V, near the redox potential of the PB⇔ES process. The changes of G_{Na} and K_{Na} with potential were determined: the equivalent diffusion coefficient of Na^+ increased when the potential became more anodic. Besides, the derivative of

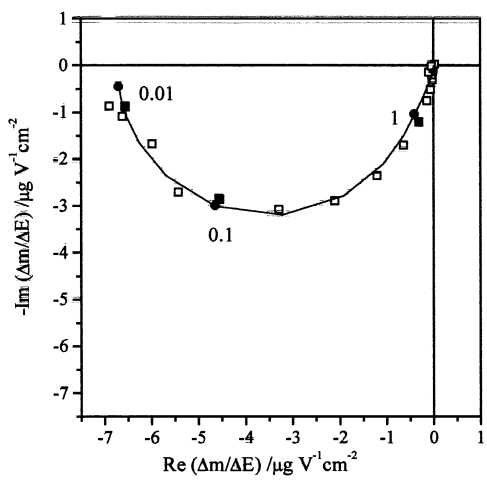

Fig. 11. Experimental electrogravimetric data (□) and simulated-fitted electrogravimetric function (—●—). $E = 0.05$ V and amorphous PB film.

insertion rates here evaluated are close to that plotted in Fig. 9 which are graphically evaluated. They were calculated by combining Eqs. (8) and (10), which leads to:

$$\frac{dC(E)}{dE} = \frac{G_{Na}}{K_{Na}} \tag{21}$$

It should be noted that the accurate value found for the atomic mass of sodium support the hypothesis about the validity of the Sauerbrey equation in the whole potential range, with a potential independant sensitivity coefficient.

6. Conclusion

Crystalline PB films can be studied in NaCl solutions by covering them with a Nafion® layer. These crystalline PB films without the presence of the protective Nafion® membrane are not stable in NaCl solution. The use of the QCM allows the atomic mass of the cations involved in the charge compensation process to be estimated. It shows that a dehydration of sodium ions takes place before they enter the PB film, decreasing the effective size of the ion and allowing their entrance into the PB film structure during the electrochemical processes. Therefore, the Nafion® membrane acts not only as a sieve that allows the transport of some ions and that prevents the transport of anions, but also participates in the electrochemical reactions allowing the dehydration of sodium ions.

The results also proved that in the case of a-PB films, sodium cations lose water molecules before they enter the film. In both cases, sodium cations are non-hydrated within PB films. This is a very interesting aspect in this study, since it could be applicable, i.e. to other electrocatalytic systems, which need the entrance of bigger hydrated ions.

The oxidation process from PB to PY is also observed in PB films covered by Nafion® layers in NaCl solutions. As the Cl^- anion transport through the Nafion® membranes is almost entirely suppressed, the electric charge compensation during the oxidation process should take place by the exit of some countercations from the film instead of the entrance of anions.

The good agreement of parameters evaluated from the fitting of impedance spectra to Eq. (19) and electrogravimetric data to Eq. (20) proves the validity of the models here proposed. By coupling these two techniques, new informations can be obtained and for example, the inserted/expelled species are identified without doubt. In addition, the kinetic parameters, G and K, can be determined at each potentials.

Table 1
Parameters evaluated from the fitting of impedance spectra data to Eq. (19) and electrogravimetric data to Eq. (21)[a]

E (V)	$m_{Na+}G_{Na+}$ [b] (μg/s per V per cm^2)	$m_{Na+}G_{Na+}$ [c] (μg/s per V per cm^2)	$\frac{K_{Na+}}{d}$ [b] (s^{-1})	$\frac{K_{Na+}}{d}$ [c] (s^{-1})	$\frac{d^2}{D_{Na+}}$ [b] (s)	$\frac{d^2}{D_{Na+}}$ [c] (s)	dC/dE [b] (mol/V per cm^3)	dC/dE [c] (mol/V per cm^3)
0.30	−17.5	−10.2	17.9	8.3	1.2	0.7	−0.28	−0.35
0.25	−31.9	−17.2	21.4	10.7	0.6	0.5	−0.42	−0.50
0.20	−31.5	−26.2	11.9	8.7	0.5	0.5	−0.78	−0.93
0.15	−33.4	−30.5	6.9	5.4	0.6	0.6	−1.50	−1.78
0.10	−24.3	−23.3	3.7	3.1	0.9	1.0	−2.04	−2.30
0.05	−12.5	−12.0	1.9	1.8	1.6	1.6	−2.07	−2.00
0.00	−4.3	−5.3	0.8	1.1	2.0	3.0	−1.64	−1.42
−0.05	−1.3	−1.8	0.4	0.8	5.4	7.8	−0.93	−0.78

[a] dC/dE represents the derivative of insertion rates evaluated such as $dC/dE = G^+_{Na}/K^+_{Na}$ and $d = 0.14$ μm.
[b] Evaluated from the electrogravimetric data.
[c] Evaluated from the electrochemical impedance data.

Acknowledgements

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