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ORIGINAL PAPER

Formation of autonomous ion sensors based on ion insertion-type materials

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Abstract We describe and discuss an integrated Li-ion sensor device combining a $LiFePO_4$ thin film prepared by pulsed laser deposition as sensing electrode and a modified ferrocene-based grafted electrode working as pseudo-reference; both were deposited onto a specific optical lithographed substrate. The simple procedure consists first of a coupling reaction at RT to form the molecule, which is grafted through a 4-h reaction with a gold substrate. Preliminary potentiometric measurements were first carried out versus a composite Bellcore electrode of $Na_{0.33}MnO_2$/C, and then with thin film electrodes of $LiFePO_4$ for the detection of Na^+ and Li^+ ions demonstrating the validity of the approach using both technologies.

Keywords Ion sensors · Integrated sensor · Thin films · Grafting

1 Introduction

The development of ion sensors for environmental or medicinal applications often requires miniaturized integrated systems. For this purpose, electrochemical detection, especially potentiometric electrode formation, is widely studied because of the simplicity of the measurements. Therefore, the relatively large size of membrane-based ion selective electrodes working with an internal reference solution has impeded the development of performing systems. Progress made in micro-electronics has contributed to the formation of new systems such as ISFETs proposed by Bergveld in the 70s [1]. At about the same time, another simple approach, namely coated wire electrodes (CWE) [2, 3], was reported but then hardly used because of intrinsic potential instabilities. Indeed in the pristine configuration of such electrodes, a thin selective membrane was directly deposited on an electronic conductor allowing planar configurations and easy integration. Basically, the sensing device can easily be miniaturized by means of various thin film elaboration techniques such as screen printing [4, 5], Pulsed Laser Deposition [6, 7], e-beam evaporation [8], RF Sputtering [9] or polymeric membrane casting for the materials incorporation. However, while the ionic equilibrium between the solid and the solution was well defined, poor definition of the electronic transfer equilibrium at the membrane/solid contact interface led to badly defined electrode potential, which drifted with time. Two ways of improving this type of electrode have been proposed. The first consists in incorporating a self-assembled mono layer (SAM) of electroactive molecules between the metal and the polymeric membrane [10, 11]. This approach is particularly appealing for organic ionophores. Another possibility is to use an inorganic mixed conductor (ionic/electronic) such as, for instance, insertion materials or ion-exchangers [12]. For several years, we explored this route aiming at quantifying Li^+ [13], Na^+ [14], K^+ [15], Cu^{2+} [16] or Ag^+ [17]. However, the development of miniaturized electrochemical sensors based on such types of material also requires incorporation of a reference electrode; the size of the measurement system must be as small as possible. This is not easy as an efficient reference electrode needs to display a rapid reversible redox couple, be non-polarizable and show a stable and reproducible equilibrium potential over time. The simple Ag/AgCl system has been one of the most studied reference

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electrodes in aqueous media and in molten salts or alcoholic solutions [18–20]. It meets the requirement by exhibiting low potential drift and good reproducibility. For planar geometries, screen printed Ag/AgCl thin or thick films [21, 22], stable and reproducible potentials were obtained by setting the chloride ion activity with KCl-based slurry. However, even using a protective polymeric matrix cover such as PVC, cellulose acetate or polyurethane [23–25] (which leaves the formation of such a reference system relatively complex), there is still some KCl dissolution leading to potential drift and solution contamination [26]. To circumvent such drawbacks, pH sensors (IrO_x [27] or MO_x [28] thin films) have been studied as pseudo-references in bio-sensors and biochip devices under development (i.e. for DNA or glucose dosing applications) used in buffered biological media. In this communication, we aim at demonstrating the feasibility of forming an autonomous integrated system by coupling a thin film sensitive part with a pseudo-reference electrode. We report the combination of PLD-made $LiFePO_4$ as Li-ion sensor or a polymeric electrode based on $Na_{0.33}MnO_2$ as Na^+ sensor with ferrocene-based grafted molecules; the ferricinium/ferrocene couple in solution can lead to the formation of stable reference systems [29] particularly recommended in non-aqueous media [30]. Whereas we would first expect such a system to be not stable and reproducible, we clearly demonstrate in this work the possibility of forming complete autonomous systems. This approach is applied here to Na^+ and Li^+ detection.

2 Characterization techniques

The electrochemical measurements were carried out in nitrate-based aqueous solutions at 25 °C. To evaluate the electrochemical activity of the grafted product, a Pt wire and a Saturated Calomel Electrode (SCE) were used as counter and reference electrodes, respectively. The electrodes were encapsulated using a silicon resin (Scotch^{TM}, 1201 Resine Silicone) leaving only the electroactive material in contact with the solution to be analyzed. Electrochemical data were recorded using a “VMP” automatic cycling/data recording system (Biologic SA, Claix, France). The grafting reaction was tested on α-Al_2O_3 substrate upon which an Au layer of around 100 nm thick was deposited by DC sputtering using a Balzer SCD40 apparatus. The potentiometric measurements were performed at 25 °C in a three-electrode configuration (tested material as working electrode, pseudo-reference and Pt grid as counter electrode). Before changing the solution concentration, we checked that the potential was stable (with a variation less than 2 mV h^{-1}).

The PLD growth of $LiFePO_4$ thin films was performed using a KrF excimer laser beam ($\lambda = 248$ nm). The growth parameters were identical to those previously reported (i.e. 10 Hz, 8×10^{-2} mBar Ar, 3 cm, 600 °C, 180 mJ) [31]. For the development of an integrated lithium ion sensor prototype, a substrate was specifically prepared using optical lithography at IEMN (Villeneuve d’Ascq, France) for the deposition of electrodes on α-Al_2O_3. It consists of two 20 nm thick Ti layers (adhesion layer) on which a 380 nm Au thin film was deposited. These two Ti/Au collectors were separated by a 200 μm gap. A Cu wire connected by a hint of silver paint to each gold collector ensured the electrical connections.

The first idea was to use the mercaptoferrocene molecule (i.e. Fc–SH), which would have been the simplest candidate for the formation of a pseudo-reference electrode. However, this is not commercially available, and its formation requires several reaction steps. We thus selected the $SH–C_6H_4–NHCO–Fc$ molecule reported by Sek et al. [10]. A simple two-step reaction was followed to enable the formation and grafting of the ferrocene-based molecule. The first step consists of a coupling reaction between 1,4 aminothiophenol ($SH–C_6H_4–NH_2$) and carboxylic acid ferrocene leading to the above described modified ferrocene molecule, with a thiol group in terminal position (Fig. 1). This coupling reaction was realized without the use of a coupling agent at room temperature (RT) in THF for 24 h. The concentration of these chemicals was 10^{-1} M. For the grafting, the gold substrate was simply left to react in the former solution for 4 h at RT and subsequently thoroughly rinsed in THF.

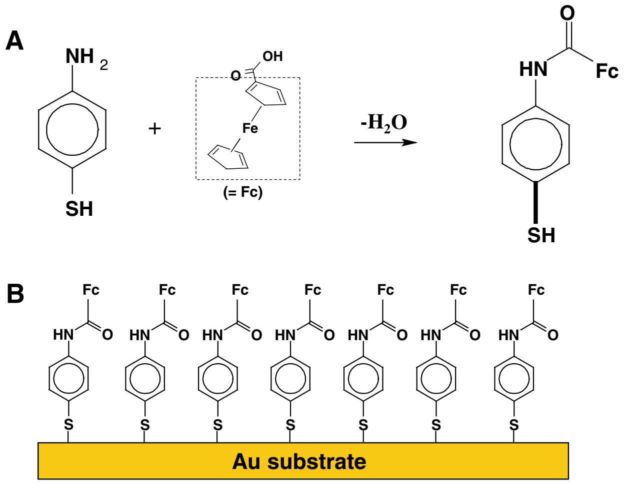

Fig. 1 (**a**) Coupling reaction between 1,4 thioaminophenol and carboxylic acid ferrocene leading at RT to a ferrocene-based molecule containing a thiol group in the terminal position (**b**) SAM of the ferrocene-based molecule upon gold

3 Results and discussion

3.1 Study of the electrochemical behaviour of the ferrocene grafted substrate versus SCE

To check the efficiency of the grafting reaction, we performed a cyclic voltammetry measurement of the gold substrate in 1 M KNO_3 at $v = 100$ mV s^{-1} sweep rate (Fig. 2). During the first oxidation, a large irreversible anodic current is observed with an onset of around $E \approx 0.30$ V vs. SCE. This phenomenon, which was systematically observed, is unclear at the present time. Further experiments are underway to better understand its origin. However, after this first oxidation sweep, the following scans obviously highlighted the presence of the signature of a redox couple ascribed to the ferrocene-based molecule grafted on the gold surface (Fig. 2b) with a formal potential of around 0.29 V vs. SCE. The higher potential compared to the simple ferricinium/ferrocene couple (0.16 V vs. SCE) is consistent with previous work showing that the amide group induces an increase in the equilibrium potential [32]. However, the current value is relatively low, thus showing that the layer formed is not compact and self-assembled. As a result of the clear redox signature, we then measured the open circuit voltage of the grafted electrode versus SCE in different media to validate its use as pseudo-reference electrode after partially oxidizing the ferrocene into ferricinium. After the electrode stabilization, whatever the electrolyte nature (nitrate of alkaline elements) and concentration, the recorded OCV evolution was stable with an O.C.V. value of *c.a.* $E \approx 0.190$ V vs. SCE. This value is lower than expected from the CV measurements reported above. Thus, several points, such as improving the grafting efficiency by means of a coupling agent and modifying the coupled molecule to increase the rapidity of the system, should be examined. This study will be reported later.

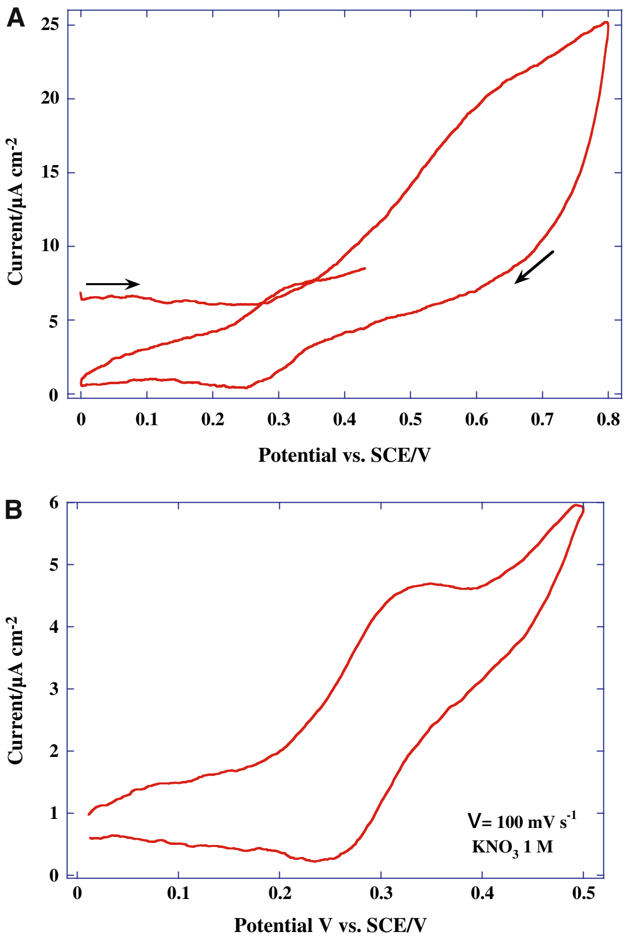

Fig. 2 Cyclic voltammetry recorded at $v = 100$ mV s^{-1} in KNO_3 1 M of a ferrocene grafted electrode for (**a**) the first cycle (**b**) the second cycle

3.2 Potentiometric study of $Na_{0.33}MnO_2$ and $LiFePO_4$ thin films versus grafted modified Fc^+/Fc

Recently, following the study by Tani and Umezawa [33], we showed the possibility of using $Na_{0.33}MnO_2$ as a sensing material for the detection of sodium when incorporated in a polymeric composite electrode using the Bellcore technology [14]. $Na_{0.33}MnO_2$/C electrodes (resulting from the oxidation of $Na_{0.44}MnO_2$ in sodium nitrate solution) exhibit a Nernstian behaviour towards Na^+ ions with a linear potential domain extending for concentrations between 1 M and 2×10^{-4} M. The sensitivity was 55 mV dec^{-1}, very close to the Nernstian response. The different investigations emphasized the relationship between the potentiometric response and Na^+ insertion/extraction mechanism underlining the importance of the presence of two-phase transitions. Similarly, such a link was also shown by a lithium insertion material, namely $LiFePO_4$, for which thin films allowed detection of lithium through a Nernstian behaviour with a detection limit as low as 10^{-4} M and a sensitivity of 54 mV dec^{-1} [34]. However, these potentiometric measurements were carried out using a commercial "macro" SCE reference electrode. The O.C.V. measured in $NaNO_3$ solution of different concentrations (Fig. 3a) is stable and evolves reversibly. The evolution is linear with the logarithm of the concentration and with a sensitivity of 55 mV per decade (Fig. 3b). These results recorded using the Fc^+/Fc couple are equivalent to those obtained with a SCE reference [14] validating the approach followed for Na^+ ion sensing. Preliminary experiments performed using a bare Au electrode (substrate used for the grafting) as a "pseudo-reference" showed that potentiometric responses could be obtained but the results were less stable and reproducible than those described above using the Fc^+/Fc

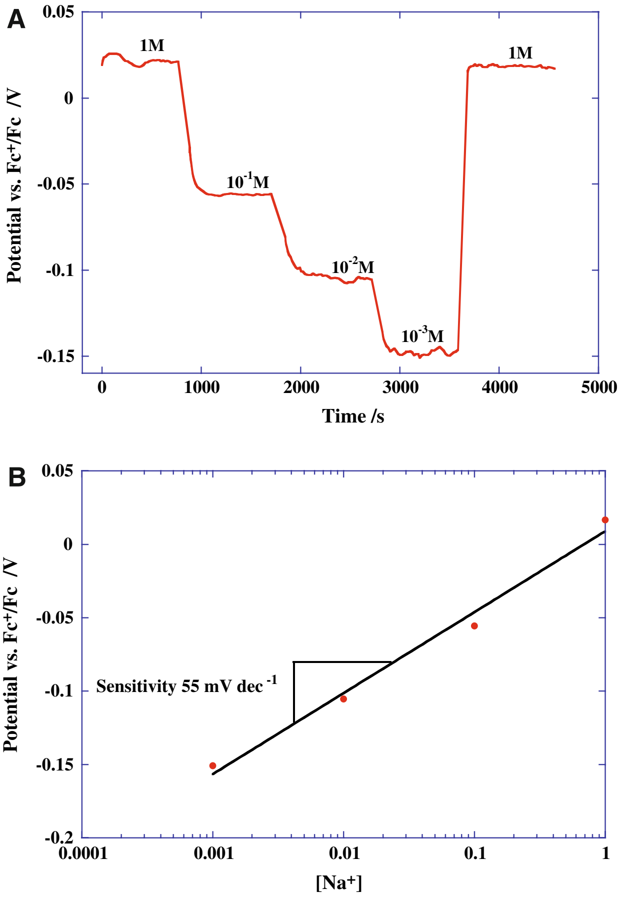

Fig. 3 (**a**) Potential evolution recorded in different $NaNO_3$ concentrations of a $Na_{0.33}MnO_2$-based composite electrode versus grafted Fc^+/Fc electrode. (**b**) Equilibrium potential recorded as a function of the logarithm of Na^+ concentration of the composite $Na_{0.33}MnO_2$ electrode versus grafted Fc^+/Fc electrode

couple. It thus underlined the beneficial effect of the grafting process for the development of integrated sensors.

3.3 Autonomic integrated lithium ion sensor device

To get closer to integration, we first tested a $LiFePO_4$ thin film-based electrode versus the Fc^+/Fc layer grafted on the α-Al_2O_3/Au substrate. Similarly to the $Na_{0.33}MnO_2$-based electrode, a stable response and good reversibility were also obtained for this lithium ion sensor. The sensitivity of the response is consistent with a Nernstian behaviour (59 mV dec^{-1}) (Fig. 4). All these results clearly stress the possibility of using the proposed approach by grafting redox molecules to create the new pseudo reference electrode. Different micro-electronic techniques such as optical lithography or electron lithography are suitable for designing of an electrode network along a well defined geometry on micro-chips. In this study, we used a particularly simple substrate presenting two parallel gold electrodes separated by a gap of 200 μm to demonstrate the potentiality of this thin film route. Thus, taking advantage of this geometry, a thin film of $LiFePO_4$ of about 400 nm thickness was grown by PLD onto the first collector while a drop of the coupled molecule was deposited onto the second gold collector for a 3-h reaction. Then, both electrodes were thoroughly rinsed with THF, and the system was encapsulated with a silicon resin to allow the active materials to be in contact only with the solution. The configuration is presented Fig. 5 with a picture of a prototype on which both the size and design of the integrated lithium ion sensor device are visible. The sensing parts were about 2 mm^2 for a whole prototype size of *c.a.* 5 × 10 mm. The first experiment was realized in cyclic voltammetry mode in $LiNO_3$ 1 M at $v = 2$ mV s^{-1} scan rate (Fig. 6b). A typical electrochemical signature of the $FePO_4/LiFePO_4$ couple is observed with a peak separation of 131 mV typical of the kinetic limitations of this system [34]. Again if we follow the evolution of the open circuit voltage for different lithium ion concentrations, stable potentiometric responses induce a linear domain usable for the quantification of lithium ion in solution, which compares well with the response obtained for both an SCE electrode and the separated electrodes (Fig. 4). Surprisingly, a higher sensitivity than previously reported for this material was noticed at a 64 mV dec^{-1} value (Fig. 6).

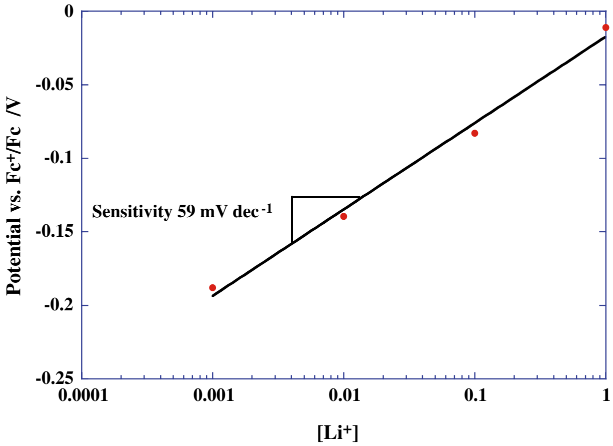

Fig. 4 Equilibrium potential recorded as a function of the logarithm of Li^+ concentration of $LiFePO_4$ thin film versus grafted Fc^+/Fc electrode

4 Conclusions

The results reported in this communication deal with the search for a way to easily produce micro-sensor devices including a pseudo reference electrode and thin film-made sensing electrode. Using a simple process, we were able to form a stable pseudo reference electrode (*c.a.* +0.190 V vs.

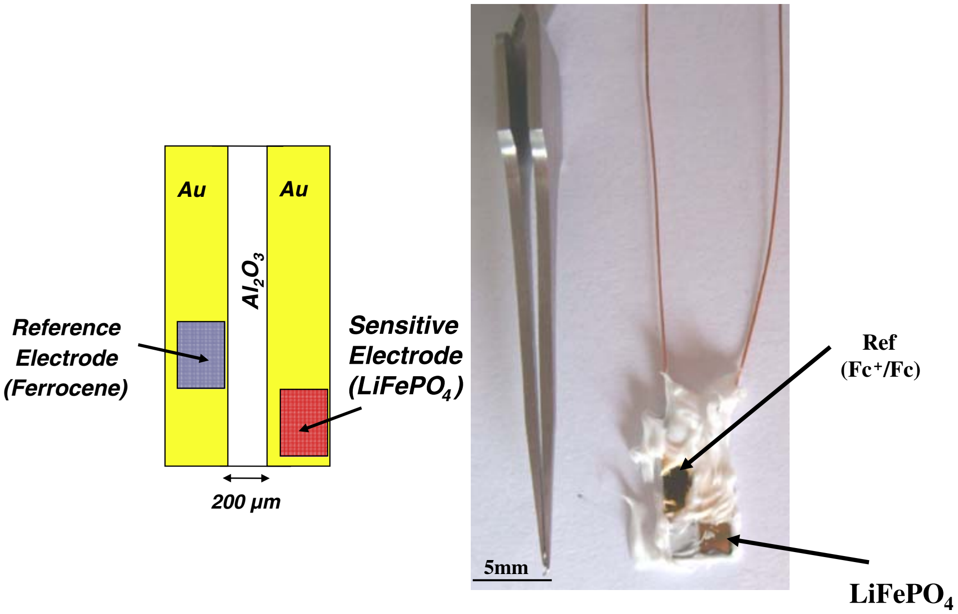

Fig. 5 Scheme and picture showing the lithium micro-sensor prototype formed with a $LiFePO_4$ thin film as sensible electrode and a grafted Fc^+/Fc pseudo-reference electrode

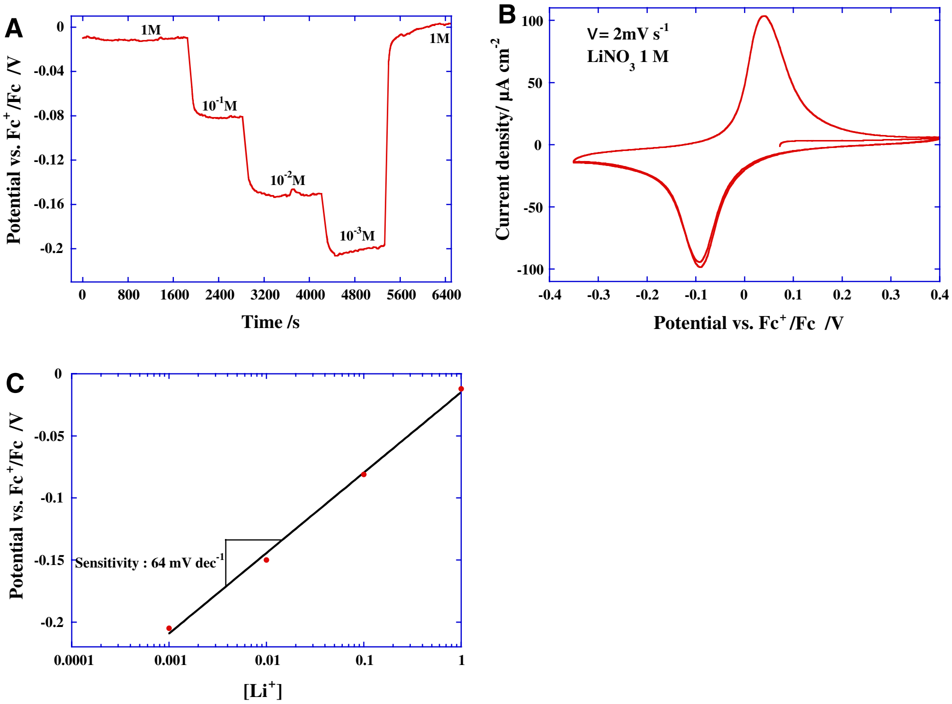

Fig. 6 (**a**) Potential evolution in $LiNO_3$ solution of different concentrations using the lithium ion micro-sensor prototype made of $LiFePO_4$ and Fc^+/Fc thin film (**b**) cyclic voltammogram of $LiFePO_4$ thin film recorded at $v = 2$ mV s^{-1} scan rate in $LiNO_3$ 1 M (**c**) Equilibrium potential recorded as a function of the logarithm of Li^+ concentration using the lithium sensor micro-device

SCE) with no influence of the tested alkaline nitrate solutions. Highly promising results were obtained versus $Na_{0.33}MnO_2$ plastic electrode and $LiFePO_4$ thin films for Na^+ and Li^+ detection, respectively. Moreover, regarding the development of micro sensor devices, we also obtained encouraging results from an integrated prototype taking advantage of the Fc^+/Fc couple and $LiFePO_4$ thin films for the detection of lithium. These preliminary results open possibilities for the development of an autonomous integrated multi-sensor; the latter could combine a pseudo- reference electrode made of a self assembled monolayer through a grafting process with thin films of a sensing material made by physical/chemical routes or following a similar grafting approach. Moreover, the well defined responses obtained in cyclic voltammetry mode show that this approach could also be extended to the formation of amperometric sensors with appropriate sensing molecules/materials. Effort is being made to further optimize the grafting process leading to SAM monolayers, and we are also studying the creation of an appropriate grafted molecule displaying higher redox rapidity. As a consequence, such an optimizing step will allow us to implement the new pseudo reference electrode to realize other prototype systems, thus keeping in mind that each system has to be specifically optimized owing to redox interferences from complex media.

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