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Conjugated redox polymer with poly(3,4-ethylenedioxythiophene) backbone and hydroquinone pendant groups as the solid contact in potassium-selective electrodes

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Abstract

We have used for the first time a conjugated redox polymer with hydroquinone (HQ) pendant groups covalently attached to the poly(3,4-ethylenedioxythiophene) (PEDOT) backbone as the solid contact (SC) in plasticized poly(vinyl chloride) (PVC) based K⁺-selective electrodes (K-SCISE). Redox couples are one of the simplest ways to precisely adjust the standard potential (E^0) of the SCISEs, but usually the initially high E^0 reproducibility is lost quite quickly due to leaching out of non-covalently bound redox molecules from the SCISE. In PEDOT-HQ, the covalently attached HQ groups prevent the leaching and simultaneously allow additional charge storage in PEDOT-HQ that is ca. 25-30 times higher than for unsubstituted PEDOT. Before the ion-selective membrane (ISM) deposition, we controlled the potential of the SC with high reproducibility (± 0.4 mV, $n=5$) by pre-polarization in a mixture of acetonitrile containing potassium tetrakis(pentafluorophenyl)borate and perchloric acid as proton source. Pre-polarization of the SC close to the formal potential where the redox

buffer capacity is highest gave the best potential reproducibility. However, after the ISM deposition, the K-SCISEs showed in the best case an E^0 reproducibility of ± 2.8 mV ($n=5$). Chronopotentiometric measurements reveal that only a minor fraction of the very high redox capacitance of PEDOT-HQ can be utilized for the ion-to-electron transduction beneath the ISM. The influence of this shortcoming on the E^0 reproducibility of the SCISEs has been underestimated for most SC materials. Modification of the commonly used PVC-ISM formulations to allow faster ion transfer at the SC/ISM interface could be one way of overcoming the disadvantage.

Keywords: Conjugated redox polymer, Poly(3,4-ethylenedioxythiophene), Hydroquinone, Covalent attachment, Standard potential, Solid-contact ion-selective electrode

1. Introduction

Potentiometry is a simple and non-destructive technique requiring only inexpensive instrumentation for measuring the electrical potential between the ion-selective electrode (ISE) and a reference electrode. The potential of the ISE is related to the ion activity of the sample solution through Nernst equation predicting a potential change of 59.2 mV/ n upon a tenfold increase/decrease of the ion activity. Today, ISE are available for ca. 100 different analytes that are mostly inorganic ions [1]. Since the introduction of electrically conducting polymer (ECP) based solid-contact ISEs (SCISE) in 1992 [2], the focus of the ISE research has shifted from the liquid contact ISEs towards SCISEs. This is due to the replacement of the liquid contact with a solid ion-to-electron transducer (solid contact, SC) facilitating miniaturization of the SCISEs [3]. Recently, the possibility of fabricating SCISEs by printing [4] on flexible and stretchable substrates [5, 6], and the possibility of incorporating SCISEs in

wearable devices for health diagnostics and sports applications, and in disposable single-use test stripes has become the biggest driving force for the SCISE research [7, 8].

Despite of many SC materials that have been recently reported [9-29], the ECPs [2, 30-32], different type of carbon materials [29, 33-36] and redox couples [37-39] are currently the most popular SC materials. Ideally, the SC should have high double layer/redox capacitance [40], electrical conductivity and exchange currents at the substrate/SC and SC/ion-selective membrane (ISM) interfaces. In addition, it must be insensitivity to light [41], oxygen and carbon dioxide [31, 42], and have high hydrophobicity to prevent the aqueous layer formation [30, 31, 43], which results in potential instability of the SCISEs [44]. While several SC fulfill many of these criteria, the researchers are still looking for the perfect SC.

There is a big demand for remote controlled and autonomous SCISEs that are maintenance-, conditioning- and calibration-free, but their commercialization has been hampered by the insufficient reproducibility of the standard potential (E^0). Even with sophisticated and often time-consuming non-robust fabrication protocols, which are tailor-made for research laboratories, it is challenging to obtain an E^0 reproducibility ≤ 3.0 mV within the same batch of SCISEs [30]. It is even more challenging to achieve high E^0 reproducibility between different electrode batches and especially for SCISEs prepared with identical preparation protocols at different research laboratories [30]. The SC plays an important role in achieving high E^0 reproducibility as it functions as an ion-to-electron transducer between the electrically conducting electrode substrate and the ionically conducting ISM. The phase boundary potential at the electrode substrate/SC and SC/ISM interfaces must be constant and reproducible to obtain SCISEs with high E^0 reproducibility. Poor reproducibility is often caused by sluggish an insufficient ion/electron transfer processes at these interfaces, diffusion of oxygen and carbon dioxide through the ISM influencing the redox state and pH of the SC [42], and partial dissolution of the SC into the ISM.

Incorporation of redox couples in the SCISEs is one of the simplest ways of improving their potential reproducibility [37, 38] as the E^0 of the SCISE can be easily tuned by adjusting the $a_{\text{ox}}/a_{\text{red}}$ ratio of the redox couple [9]. However, the initially very good E^0 reproducibility is often (± 0.7 mV, $n=5$ [38]) deteriorating rather quickly because non-covalently bound redox compounds easily leach out to the sample solution. In contrast to redox couples, the ECPs have a broad distribution of energy levels due to polymer segments with different conjugation length, making it challenging to fabricate SCISEs with satisfactory E^0 reproducibility. Therefore, the SC must be pre-polarized at a potential located in the conducting regime to improve the potential reproducibility of the ECP based SCISEs [30, 31, 41, 43].

Conjugated redox polymers (CRP) are a relatively new class of ECPs in which redox groups are covalently attached via linkers to the ECP backbone, thus preventing them from leaving the backbone [45, 46]. Especially the modification of polypyrrole (PPy) [47-55] and PEDOT [56-64] with redox pendant groups have received much attention. One of the most successful approaches is the covalent modification of PEDOT with hydroquinone (HQ) pendant groups (Scheme 1) [61, 62]. In contrast to PPy, the stiffer PEDOT backbone prevents it from twisting upon the reversible HQ to benzoquinone (BQ) redox conversion, the twisting has been shown to decrease the number of charge carriers in PPy and therefore decreasing its electrical conductivity [50, 51]. PEDOT-HQ has excellent redox matching with the HQ/BQ redox conversion occurring in the potential region where PEDOT is in its electrically conducting form, which is necessary for obtaining a synergistic effect between the polymer backbone providing fast electron transport through the PEDOT matrix and the HQ groups offering a large charge storage capacity [61]. Estimations show that 12% of the capacitance of PEDOT-HQ originates from its backbone and 88% from the HQ pendant groups [61]. Most importantly, the HQ pendant groups provide PEDOT-HQ with a well-defined redox reaction

that has been explored in this work. At neutral pH, where the SCISEs are usually used, the oxygen transported by water to the SC/ISM interface cannot oxidize HQ to BQ due to the lower standard potential of the oxygen half-cell [39, 65], and therefore minimizing the risk for potential instability caused by changes in the $a_{\text{HQ}}/a_{\text{BQ}}$ ratio.

(Scheme 1)

To the best of our knowledge, we are not aware of any similar works where CRPs have been applied as ion-to-electron transducers in SCISEs. We have used PEDOT-HQ as a model compound to study its influence on the initial potential stability and E^0 reproducibility of K^+ -selective SCISEs (K-SCISE). Prior to the ISM deposition, the potential of the PEDOT-HQ solid contact could be controlled very precisely (± 0.4 mV, $n=5$) by pre-polarization in a mixture of acetonitrile (MeCN) containing 0.01 M potassium tetrakis(pentafluorophenyl)borate (KTFAB) and perchloric acid (HClO_4) acting as a proton source for the HQ groups. However, the E^0 deviation of the K-SCISE increased to ± 2.8 mV ($n=5$) indicating that the ISM deposition influences the potential reproducibility [31]. The K-SCISEs prepared with PEDOT-HQ pre-polarized in 0.01 M KTFAB-MeCN without HClO_4 had excellent initial potential stability with a potential drift of only ca. 0.1 mV h^{-1} during 24 h. PEDOT-HQ solid contacts and the corresponding K-SCISEs have been characterized with the state-of-the-art techniques.

2. Material and methods

2.1 Chemicals

EDOT-HQ was custom-synthesized according to the recently published procedure [61]. High-molecular weight PVC (HMW PVC), bis(2-ethylhexyl) sebacate (DOS), potassium ionophore

I (valinomycin), and tetrahydrofuran (THF), and anhydrous acetonitrile (MeCN) (99.5%) were purchased from Sigma-Aldrich, and potassium tetrakis(pentafluorophenyl)borate (KTFAB) (97%) from Alfa Aesar. Buffer solution for the electrochemical characterization of the PEDOT-HQ solid contact were prepared from sodium nitrate, sodium acetate, monobasic sodium phosphate, boric acid (all from Sigma-Aldrich) and the pH was adjusted to 0 and 5.5 with HNO₃. The chloride salts (K⁺, Na⁺, Ca²⁺, Mg²⁺, NH₄⁺, Li⁺, H⁺) used for the potentiometric and impedance measurements had a purity > 99%. Perchloric acid (70 v/v%) was received from Sigma-Aldrich. The aqueous solutions used in this work were prepared from deionized water (DIW) that had a resistivity of 17 MΩcm.

2.2 Characterization of the K-SCISE substrates and electropolymerization of EDOT-HQ

The glassy carbon (GC) electrodes incorporated in insulating polyether ether ketone (PEEK) bodies had a diameter of 1.6 mm (BioLogic) and were used as electrode substrates for the K-SCISEs. The electrochemical response of the GC electrodes ($n=5$) were measured in 2 mM K₄Fe(CN)₆ with 1.0 M KNO₃ as the supporting electrolyte prior to the electropolymerization of the solid contact on top of them. Prior to the electropolymerization, the WE was polished with a 0.05 μm alumina suspension, rinsed thoroughly with ethanol and DIW followed by ultrasonication for 5 min in DIW, and finally rinsed again with ethanol and DIW. The electropolymerization of 5 mM EDOT-HQ in a 0.01 M KTFAB-MeCN solution was performed in a three-electrode cell (3 mL) with an Autolab potentiostat by cycling the potential 10 times between – 0.3 and 1.4 V with a scan rate of 50 mV s⁻¹. The GC disc electrodes, a Pt wire and Ag wire immersed in 0.01 M AgNO₃ and 0.1 M TBAPF₆ dissolved in MeCN (vs. Ag/Ag⁺) served as working (WE), counter (CE) and reference electrode (RE), respectively. Due to the limited amount of the EDOT-HQ monomer, we performed five electropolymerizations from the same monomer solution and purged the solution with MeCN

saturated N₂ gas for 5 min prior to each electropolymerization. The solution was blanketed with N₂ during the electropolymerization to protect it from oxygen (air). After the polymerization, we washed the PEDOT-HQ electrodes with MeCN and stored them under inert argon gas.

2.3 Characterization of the PEDOT-HQ solid contact

The PEDOT-HQ films were characterized with cyclic voltammetry (CV; $v=5, 10, 20, 50$ and 100 mV/s) in 1.0 M NaNO₃ buffered to pH 0 and 5.5 with sodium acetate, monobasic sodium phosphate and boric acid (0.1 M each, pH was adjusted with concentrated HNO₃). All measurements were performed using the three-electrode setup at an ambient temperature with Ag/AgCl/3M KCl and a Pt wire as the RE and CE, respectively. We studied the surface morphology of the PEDOT-HQ solid contacts with scanning electron microscopy by using the LEO1530 Gemini FEGSEM instrument. The light sensitivity measurements of the PEDOT-HQ film were carried out in 1.0 M KNO₃ by exposing them to room light, darkness and to cold light (Leica CLS 150XE light source, $>1.6 \times 10^5$ lx) for 30 min each in this sequence, and simultaneously recording the potential of the film electrodes [41]. To determine the redox capacitance of PEDOT-HQ, the electrochemical impedance spectra were measured in buffered aqueous solutions at pH 0 and 5.5 (see above) in the frequency range from 0.01 Hz to 10 kHz at the open circuit potential (vs. Ag/AgCl/3M KCl) with $\Delta E_{ac}=5$ mV. The water contact angles (WCA) of PEDOT-HQ was measured for films that had been pre-polarized for 2 min at 0.0 V and 0.55 V in 1.0 M KNO₃ (pH 5.5), and dried with N₂ gas after the pre-polarization. We applied a water droplet of 2 μ L on the PEDOT-HQ surface and recorded images of the droplet with the Dyno-Lite USB digital microscope. The WCAs were estimated from the images with the Inkscape 0.92.3 software. The potentiometric ionic response of the

PEDOT-HQ film was determined in 10^{-1} - 10^{-4} M KCl and 10^{-2} - 10^{-5} M KTFAB (dissolved in MeCN).

2.4 Pre-polarization of the PEDOT-HQ solid contact and the ISM deposition

Prior to the ISM deposition by drop casting, we pre-polarized simultaneously five identically prepared PEDOT-HQ solid contacts for 5 min at 0.25 V either in a 9:1 (v/v%) mixture of 0.01 M KTFAB-MeCN and 0.2 M HClO₄ (acting as a proton source for the HQ groups) or in 0.01 M KTFAB-MeCN without HClO₄. This was done to improve the E^0 reproducibility of the K-SCISEs [30, 31, 41, 43]. After the pre-polarization, the PEDOT-HQ solid contacts were dried under N₂ atmosphere for 30 min before drop casting the ISMs on top of the SCs. The ISM had the following composition (wt%): 32.9% HMW PVC, 65.7% DOS, 1.06% valinomycin and 0.34% KTFAB. All components were dissolved in 1 mL THF to produce a solution with a dry weight of 20%. The solution was first vortexed for 3 min and was then left on gentle stirring on a shaking table for 24 h to dissolve the ISM components in THF. Finally, 40 μ L of the K⁺-selective ISM cocktail was drop cast on the PEDOT-HQ in two consecutive steps (2 \times 20 μ L). After drying overnight under THF atmosphere, the PVC-ISM had a thickness of ca. 220-240 μ m.

2.5 Characterization of the K-SCISEs

We used a 16-channel high input impedance voltmeter with the input impedance of 10^{15} Ω , (Lawson Laboratories, Malvern, PA, USA) in all potentiometric measurements. The initial potential stabilities of the K-SCISEs were determined in 0.01 M KCl for 24 h. The K-SCISEs were calibrated from 10^{-1} to 10^{-9} M KCl, and the potential readings at each concentration were taken after 5 min in quiescent solutions (stirring during the first 3 min). The potentiometric aqueous layer test was done with fully conditioned SCISEs by changing the

solution from 0.1 M KCl (3 h) to 0.1 M NaCl (24 h) and then back to 0.1 M KCl (24 h). The gas sensitivity of the K-SCISE was determined by measuring the electrode potential while purging a 0.1 M KCl solution with pure gases in the following sequence: N₂ (30 min), O₂ (30 min), N₂ (ca. 35 min), CO₂ (50 min), N₂ (45 min). We determined the potentiometric selectivity coefficients of the K-SCISEs with the separate solution method in 0.1, 0.01 and 0.001 M chloride salts of K⁺, and the interfering ions Li⁺, Na⁺, H⁺, NH₄⁺, Ca²⁺ and Mg²⁺. We used Ag/AgCl/3 M KCl//1 M LiOAc as the RE in all these measurements described above. The chronopotentiograms were recorded with an Autolab potentiostat in 0.1 M KCl by applying first a current of 10⁻⁹ A for 60 s and -10⁻⁹ A for the next 60 s. The impedance spectra of the K-SCISEs were measured in the frequency range of 0.01 Hz - 25 kHz at the open circuit potential with $\Delta E_{ac}=0.1$ V. Ag/AgCl/3 M KCl was used as the RE in the two last measurements.

3. Results and Discussion

3.1 PEDOT-HQ solid contact

Surface functional groups (carbonyl, carboxyl, and hydroxyl) can affect the electron transfer property of the GC electrode substrates used for the K-SCISEs [66]. Therefore, we measured the CVs of the GC electrodes in 2 mM K₄Fe(CN)₆ with 1.0 M KNO₃ as the supporting electrolyte to study their reversibility. The CVs of four identical electrodes in Figure S1 reveal that the electron transfer is reversible with a peak separation of 69.4±2.6 mV, which is close to the theoretically predicted value of 59.2 mV (25°C) for a one electron redox process (Table S1). Figure S1 shows also that the anodic and cathodic peak potentials ($E_{pa}=300.4\pm0.1$ mV and $E_{pc}=231.0\pm2.5$ mV) had high reproducibility contributing to a high E^0 reproducibility of the K-SCISEs.

The electropolymerization of 5 mM EDOT-HQ was carried out by cyclic voltammetry in a MeCN solution containing 0.01 M KTFAB with high fluorine content to enhance the hydrophobicity of the PEDOT-HQ solid contact (Figure S2). Figure S3 shows the CVs recorded during the electropolymerization of three identical PEDOT-HQ films from the same monomer solution. Almost the same currents that were observed in the CVs reveal that the electropolymerization is reproducible. The monomer oxidation peak at 1322 ± 12 mV ($n=3$; 10th cycle) indicates that the PEDOT-HQ film grows in the potential interval of ca. 1.1 - 1.4 V (vs. Ag/Ag⁺), while the oxidation/reduction of the PEDOT backbone and the HQ pendant groups (Scheme 1) occur in the interval of -0.3 - 1.1 V. As the PEDOT backbone is in its electrically conducting form already at low potentials, it provides a good redox match for the HQ/BQ redox conversion that has the oxidation and reduction peak potentials at 1032 ± 16 mV and 188 ± 23 mV, respectively. The SEM image in Figure S4 reveals that the surface of the PEDOT-HQ solid contact prepared in the presence of the TFAB⁻ anions is rather smooth and compact with some larger sections sticking out from surface. We expected that a compact surface is beneficial for SCs because it prevents the pores of the SC from being filled with water diffusing through the ISM. It has been shown that the diffusion of water through the ISM promotes the water layer or pool formation at the SC/PVC-ISM interface [67], which causes response instability of the SCISEs [44].

Scheme 1 shows the reversible oxidation and reduction of the PEDOT backbone and the HQ pendant groups. The oxidation of the PEDOT backbone that occurs first at lower potentials results in the formation of charge carriers that make the polymer backbone electrically conducting. To fulfill the electroneutrality condition of PEDOT, the oxidation of the backbone is accompanied by the insertion of charge compensating TFAB⁻ anions, which are also present in the ISM to stabilize the phase boundary potential at the SC/ISM interface. The high charge storage capacity of PEDOT-HQ is due to the HQ groups that can store two

electrons in every repeating EDOT unit of the polymer (Scheme 1), in comparison to only ca. 0.4-0.6 electrons for every EDOT unit in the polymer backbone [68] depending on its oxidation degree and nature of the charge compensating counterion.

In buffered aqueous solutions, the HQ/BQ redox reaction is a $2e^- 2H^+$ reaction with two coupled electron-proton transfer reactions close to each other in formal potentials (E^0), which usually gives one overlapping oxidation/reduction peak in the CV of HQ/BQ [69]. Figure 1a shows therefore only one broader oxidation/reduction peak in the CV of PEDOT-HQ measured at pH 0. In PEDOT-HQ, the two step oxidation process of HQ to BQ has been proposed [62] to proceed first via electron transfer from HQ (denoted as H_2Q in [62]) to the PEDOT backbone forming semiquinone radicals (H_2SQ^+), which are then deprotonated to neutral HSQ. In the second step, HSQ is further oxidized either via the HQ^+ or SQ^- intermediates to the fully oxidized benzoquinone. Due to the very high currents of the HQ/BQ redox conversion, the much smaller oxidation/reduction currents of the PEDOT backbone cannot clearly be distinguished in Figure 1a. However, the difference in the redox currents of PEDOT-HQ and unsubstituted PEDOT at pH 0 is shown in Figure 2 illustrating the huge influence of the HQ pendant groups on the redox currents of PEDOT-HQ.

(Figure 1a and 1b)

(Figure 2)

Figure 1a reveals that the redox peak separation (ΔE_p) of the PEDOT-HQ film measured with the scan rates of 5 mV s^{-1} was 31.0 mV, which is slightly higher than expected for a surface confined reaction (0 mV). The HQ/BQ peak separation increased slightly at higher scan rates ($\Delta E_p=98.9 \text{ mV}$ at 100 mV s^{-1}) indicating that the electron transfer becomes kinetically somewhat more sluggish. However, the formal potential (E^0) of the HQ/BQ redox

reaction varies only between 505.5 – 514.2 mV and is practically independent of the scan rate, which further confirms the high reversibility of the HQ/BQ conversion in PEDOT-HQ electropolymerized in the presence of KTFAB. Since the SCISEs are usually used in neutral or slightly acidic solutions, we have also studied the reversibility of the HQ/BQ redox conversion at pH 5.5. We assume that the pH at the SC/ISM interface in the K-SCISEs is ca. 5.5 because water that is saturated with CO₂ can easily diffuse through the PVC-ISM to the SC [70]. In Figure 1b, the CVs of PEDOT-HQ measured at pH 5.5 show lower redox currents and higher peak separation ($v=5-20 \text{ mV s}^{-1}$) than at pH 0. Since two protons are involved in the HQ/BQ redox reaction, an increase in pH should shift the oxidation/reduction peaks to lower potentials with 59.2 mV/one pH unit (at 25°C). Indeed, the $E^{0'}$ shifts to a lower potential with 325.5 mV ($v=20 \text{ mV s}^{-1}$) when pH increased from 0 to 5.5, which is in perfect accordance with the theoretical prediction of 325.6 mV. The higher peak separation at pH 5.5 indicates that the electron transfer kinetics becomes more sluggish. This is in agreement with the theory for proton coupled redox reactions where the apparent standard rate constant (k_s) is expected to reach a minimum at a pH midway between the pK_a of the oxidized and reduced species [71]. At the higher scan rates (50 and 100 mV s^{-1}), the HQ/BQ redox peak splits into two peaks indicating that the second redox reaction is kinetically slower than the first due to the radical disproportionation despite of its higher driving force. This result in a higher difference of the $E^{0'}$ values associated with the two processes involved in the $2e^- 2H^+$ oxidation/reduction. Despite of the kinetically slower redox conversion at pH 5.5, the ratio of the integrated oxidation peak areas at pH 5.5 to pH 0 is ca. 1.3 and ca. 24.9 between PEDOT-HQ at pH 5.5 and unsubstituted PEDOT (Figure 2a), showing that PEDOT-HQ is most suitable as an ion-to-electron transduction in SCISEs.

To determine the redox capacitance that should be high for the SC, we measured the electrochemical impedance spectra of the PEDOT-HQ films at pH 0 ($E_{dc} = 0.30, 0.55$ and 0.70

V) and pH 5.5 ($E_{dc} = 0.00, 0.30$ and 0.55 V). The measurements were performed at the potentials given in the parenthesis corresponding to DC potentials before the HQ/BQ oxidation peak, at the peak and after the peak (cp. Figure 1a and 1b; $v=20$ mV s⁻¹). The redox capacitance of the films was estimated from the low frequency part of the impedance spectra shown in Figure S5a and S5b by assuming that they have an almost capacitor-like behavior. The capacitances were determined from the $|-Z''|$ vs. f^{-1} relationship by line fitting ($y=ax$) and calculating the capacitance from the slope (a) of the straight line ($C = (2\pi a)^{-1}$) [72]. The estimated redox capacitances of PEDOT-HQ were 43 (0.30 V), 489 (0.55 V) and 18 mF cm⁻² (0.70 V) at pH 0, and 66 (0.00 V), 123 (0.30 V) and 15 mF cm⁻² (0.55 V) at pH 5.5. For both pH 0 and 5.5, we obtained the highest redox capacitances when we measured the impedance spectra at a DC potential corresponding to the current maximum of the HQ/BQ oxidation peak. At these potentials, the applied AC potential (ΔE_{ac}) is able to induce an oxidation/reduction of the pendant HQ groups that is reflected as a higher redox capacitance of PEDOT-HQ. This is not possible at the lowest potentials where the amplitude of the AC potential (5 mV) is not enough to oxidize HQ to BQ to any greater extent. At the highest DC potential (0.55 V), the impedance spectrum measured at pH 5.5 shows almost a vertical capacitor-like behavior indicating that the HQ oxidation is completed and the applied AC potential is too low to reduce BQ back to HQ. Hence, we can assume that at 0.55 V only the PEDOT backbone contributes to the estimated redox capacitance of 15 mF cm⁻².

Ideally, the conducting polymer SCs should not respond to changes in the illumination conditions. Therefore, we measured the potential response of the PEDOT-HQ solid contact when it was exposed to room light, darkness and intense cold light (Figure 3). No light sensitivity was observed to room light and darkness, but a very minor response (< 2 mV) to intense cold light (1.6×10^5 lux). However, the SCISEs are never exposed to such extreme conditions and we can conclude that PEDOT-HQ is in practice insensitive to light.

(Figure 3)

2.2 K^+ -selective SCISEs

The pre-polarization of the SC prior to the ISM deposition on top of it has become a common practice to improve the potential reproducibility of the ECP based SCISEs [29-31, 41, 43]. This is usually done in organic electrolyte solutions to avoid exposing the SC to water that can cause potential drift of the SCISE. Therefore, we did the pre-polarization first in 0.01 M KTFAB-MeCN solution (Figure S6). The CV of PEDOT-HQ shows only one broad HQ oxidation peak at $E > \text{ca. } 0.5 \text{ V}$ during the first potential cycle, but no reduction peak. During the HQ oxidation, the protons are lost by diffusion to the bulk of the MeCN solution and due to the absence of protons in the aprotic MeCN, BQ cannot be reduced back to HQ via the $2e^- 2H^+$ reduction process. In aprotic solvents such as MeCN, the reduction of benzoquinone is known to proceed instead via a reversible two-electron process through the Q^- intermediate to the fully reduced Q^{2-} (Scheme S1) [69]. However, in the absence of protons that stabilize the reduced form of PEDOT-HQ, the formal potential is considerably lower than in acidic solutions [73] and thus the redox reaction occurs usually at potentials where the PEDOT backbone is electrically non-conducting. Therefore, the redox peaks cannot be observed in the CV. We found that it was possible to restore the oxidation and reduction peaks of HQ/BQ in the CV by adding 0.2 M HClO_4 as a proton source ($\text{pK}_a = 2.1$ in MeCN [74]) to the 0.01 M KTFAB-MeCN solution (Figure S6). In a 10:1 (v/v%) mixture of 0.01 M KTFAB-MeCN and 0.2 M HClO_4 , the CVs showed high redox currents with a $E^{0'}$ of ca. 228 mV for the HQ/BQ redox conversion of PEDOT-HQ. We have used therefore a 9:1 mixture of 0.01 M KTFAB-MeCN and 0.2 M HClO_4 (10 v/v%) for the pre-polarization of the PEDOT-HQ solid contact to 0.25 V prior to the ISM deposition by drop casting. In addition, we have pre-polarized the SC to the same potential in only 0.01 M KTFAB-MeCN (without HClO_4) to study how the

absence of HClO_4 influences the initial potential stability and E^0 reproducibility of the K-SCISEs.

We pre-polarized simultaneously five identical PEDOT-HQ solid contacts for 5 min at 0.10, 0.15, 0.20, 0.25 and 0.30 V (vs. Ag/Ag^+). After the pre-polarization, we measured their open circuit potentials for 5 min in the pre-polarization solutions to evaluate the robustness of the pre-polarization. Figure 4 shows that the PEDOT-HQ films pre-polarized in the 9:1 solution mixture at 0.20 V and 0.25 V had open circuit potentials with the lowest standard deviation (SD) of only 0.6 mV and 0.4 mV, respectively. This confirms that we can precisely control the potential of the PEDOT-HQ solid contact in a robust way with pre-polarization. The pre-polarization potentials are very close to the formal potential of the HQ/BQ pendant groups in the 9:1 mixture (0.228 V) where $a_{\text{HQ}}/a_{\text{BQ}} = 1$, which should give the best redox buffering capacity counteracting processes influencing the electrode potential. The PEDOT-HQ films pre-polarized only in 0.01 M KTFAB-MeCN (without HClO_4) had also the lowest SD of the measured potentials at 0.20 V and 0.25 V (2.6 mV and 2.3 mV), but in general, the potential reproducibility was worse (2.3 - 8.0 mV) compared to pre-polarization in the 9:1 mixture. We believe that the lower reproducibility is due to the difficulty in adjusting the redox state of the HQ pendant groups in the absence of protons in an aprotic solvent.

(Figure 4)

(Figure 5)

The initial stability of the K-SCISEs measured for 24 h in 0.01 M KCl is shown in Figure 5. The K-SCISEs prepared with the PEDOT-HQ solid contact pre-polarized at 0.25 V in the 9:1 mixture of 0.01 M KTFAB-MeCN and 0.2 M HClO_4 (K-SCISE_{mix}; curve b) had a relatively high initial potential drift for ca. 40 min when the electrodes were for the first time

contacted with 0.01 M KCl. After that, the potentials drifted slowly towards lower potentials with a speed of -2.8 mV h^{-1} . The initially rather high potential irreproducibility of $\pm 16.0 \text{ mV}$ ($n=5$) decreased to $\pm 9.3 \text{ mV}$ in the end of the initial potential stability test. For the K-SCISEs that had a PEDOT-HQ solid contact pre-polarized at 0.25 V in only 0.01 M KTFAB-MeCN (K-SCISE_{org}; curve a), we observed a potential drift of ca. 4-5 mV during the first 30 min, but after that a very low drift of 0.1 mV h^{-1} during the rest of the test period of 24 h, similar to the liquid contact ISEs. However, the electrodes showed a low initial potential reproducibility of $\pm 21.2 \text{ mV}$ ($n=5$) that was practically unchanged after 24 h in 0.01 M KCl ($\pm 19.0 \text{ mV}$). The relatively high potential irreproducibility of both K-SCISE types indicate that the ISM deposition process affects negatively the initially very good potential reproducibility of the PEDOT-HQ solid contacts ($\pm 0.4 \text{ mV}$ and $\pm 2.3 \text{ mV}$). We have recently observed the same for K-SCISEs that have a SC consisting of highly hydrophobic fluorinated PEDOT (PEDOT-F) [31]. In all cases when we did the pre-polarization of the SC in the aqueous-organic solvent mixture, the initial potential drift of the K-SCISE_{mix} was higher than for the K-SCISE_{org}. It may indicate that there is a correlation between the presence of water in the pre-polarization solution and the higher initial potential drift of the SCISEs. In addition, it is likely that the perchlorate anions will function as secondary doping ions for the PEDOT backbone during the pre-polarization in the 9:1 mixture. We speculate that this may contribute to time-dependent changes (instability) in the phase boundary potential at the SC/ISM interface, which is reflected as the slow drift (-2.8 mV h^{-1}) during the initial potential stability test in Figure 5 (curve b). Potentiometric measurements in $10^{-5} - 10^{-2} \text{ M}$ KTFAB dissolved in MeCN showed that the PEDOT-HQ solid contact had an anionic response of ca. -50 mV/decade indicating that it primarily exchanges anions. Therefore, the anion exchange of the SC must be accompanied by a release/uptake **TFAB⁻ anions** at the SC/ISM interface to compensate for

any oxidation and reduction changes occurring in the backbone of the PEDOT-HQ solid contact during the potentiometric measurements.

The water contact angles (WCA) of the PEDOT-HQ films pre-polarized at 0.0 V and 0.55 V at pH 5.5 were ca. 70° and 60°, respectively, showing that the polymer backbone interacts with water. Compared to PEDOT-F with a WCA of 133° [31], the WCA reveals that PEDOT-HQ is more hydrophilic, which is most likely due to the hydrophilicity of the HQ pendant groups. On the other hand, the very high initial potential stability of the K-SCISE_{org} (with absence of water in the pre-polarization solution) indicate that the lower hydrophobicity of the PEDOT-HQ solid contact, incorporating the hydrophobic TFAB⁻ anions, does not have a negative impact on the potential stability of the K-SCISEs. However, despite of the intensive research activity for almost three decades [1], more research is still needed to reach a general understanding and consensus about factors governing the potential stability and reproducibility of the SCISEs.

In Figure 6, the calibration curves of the K-SCISEs measured in 10⁻⁹-10⁻¹ M KCl after the initial potential stability test show that both types of K-SCISEs had a highly reproducible Nernstian slope (60.8±0.1 and 60.9±0.1 mV pK⁻¹, *n*=5) and a detection limit of ca. 2×10⁻⁷ M, which is typical for PVC based SCISEs. The *E*⁰ of the electrodes were determined from the calibration curves by extrapolation of the linear potential response to *a*_K=1 (i.e. log *a*_K=0). Figure 6 reveals that the K-SCISE_{org} had a high *E*⁰ irreproducibility of ±18.6 mV (*n*=5), which did not decrease from the initial potential stability test in Figure 5 (curve a), whereas the K-SCISE_{mix} showed a high *E*⁰ reproducibility of ±2.8 mV (*n*=5) that is much lower than in Figure 5 (curve b).

(Figure 6)

Although the reason for the converging potentials of K-SCISE_{mix} is still unknown, it is probably due to the presence of HClO₄ and/or water in the pre-polarization solution of the PEDOT-HQ solid contact. Because all K-SCISEs had the same ISM thickness of ca. 220-240 μm , it is reasonable to assume that the same amount of water will be present at the SC/ISM interface in both K-SCISE types after being in contact with 0.01 M KCl for 24 h (because of diffusion of water through the ISM) [67]. Indeed, the aqueous layer test shown in Figure 7 confirms the presence of water at the inner interfaces of both K-SCISE types (only K-SCISE_{mix} shown). Dissolved O₂ and CO₂ are transported to the SC with water, but the gas sensitivity test in Figure 8 demonstrates that the K-SCISEs were practically insensitive to these gases and we can therefore exclude that they are causing the potential drift observed for the K-SCISE_{mix} in Figure 5 (curve b). We want to stress that we did not study the long-term potential (E^0) stability and reproducibility in this work. However, the convergence of the potential of the K-SCISE_{mix} during the first 2 days that they were in contact with KCl solution (Fig. 5 and 6) indicates that the electrodes short-term potential reproducibility improves by time, but also that the HQ pendant groups stay covalently attached to the PEDOT backbone. As this paper focuses largely on fundamental aspects of the PEDOT-HQ as a new SC material for K-SCISEs, a separate study should be devoted to the optimization of the long-term potential stability and reproducibility of the K-SCISEs.

(Figure 7)

(Figure 8)

The logarithmic selectivity coefficients of the K-SCISEs for the most relevant interfering ions shown in Table S2 were between -4.2 to -6.7 (except NH₄⁺, -1.7), which is in rather good accordance with K-SCISEs having the same ISM composition [30, 31] confirming the high selectivity of the ISM. Further characterization of the ISM with

impedance spectroscopy revealed that its bulk resistance (R_b) varied between ca. 4-7 M Ω (determined from the diameter of the semicircle). However, the low frequency (capacitive) tail in the impedance spectrum in Figure S7 indicates some sluggishness in the electron transfer at the SC/electrode substrate interface, which probably contributes to the peak splitting and higher peak separation of the HQ/BQ redox peaks observed in the CVs measured at pH 5.5 (Figure 1b). We estimated the redox capacitance of the PEDOT-HQ solid contact buried beneath the PVC-ISM from the chronopotentiograms shown in Figure S8. The results reveal that the K-SCISE_{mix} and K-SCISE_{org} had a redox capacitance of 1.1 and 1.5 mF cm⁻², respectively, showing that only a minor fraction of the initially very high redox capacitance of the PEDOT-HQ film can be utilized beneath the ISM. Although Bobacka has previously showed that the redox capacitance of PEDOT is lower beneath the ISM [40], the results presented here demonstrate the drastic decrease of the available redox capacitance more clearly than before. In case of PEDOT-HQ, it is most likely due to the insufficient ion transfer at the SC/ISM interface preventing an efficient oxidation/reduction of the PEDOT backbone, but also because of deficiency of protons hindering the redox conversion of the pendant HQ groups. We note that the redox capacitances of 1.1 and 1.5 mF cm⁻² are still high enough to prevent any considerable changes in the a_{HQ}/a_{BQ} ratio that could be reflected as a potential drift of the K-SCISEs under normal operational conditions. This is because the currents in high input impedance voltmeters are in pA range or below, whereas the K-SCISEs in Figure S8 have been polarized with much higher currents ($\pm 10^{-9}$ A). We can conclude that the composition of the commonly used PVC-ISM might not be the most suitable for the SCISEs. They would benefit from ISMs with higher ion mobilities that facilitate a faster ion transfer at the SC/ISM interface and in addition, match the charge compensating ion transfer process associated with the redox reaction of the conducting polymer SC. In most cases, the PVC-ISM formulations developed for the liquid contact ISEs have been adopted for the SCISEs as

such. Hence, we believe that more efforts should be directed in further optimization of their composition or in finding substitutes for the PVC-ISMs.

5. Conclusions

We have used for the first time the redox conjugated polymer (PEDOT-HQ) with covalently attached HQ pendant groups as the ion-to-electron transducer (solid contact) in K^+ -selective SCISEs. Due to the HQ pendant groups, the redox capacitance of PEDOT-HQ (ca. 490 mF cm^{-2} at pH 0) is superior to unsubstituted PEDOT. With covalent attachment of the redox groups to the polymer backbone, we overcome the usually encountered problem of leaching out of the non-covalently bound redox groups from the SC or ISM, which gives rise to potential drift and potential irreproducibility of the SCISEs. In the best case, we obtained the E^0 reproducibility of only ± 2.8 mV ($n=5$) for the K-SCISEs that had been conditioned in 0.01 M KCl for 24 h. We show also that pre-polarization of the SC in a water-free 0.01 M KTFAB-MeCN (prior to the drop casting of the ISM) gave K-SCISEs with a very low initial potential drift of only 0.1 mV h^{-1} , but higher E^0 irreproducibility. Our results indicate that the presence of $HClO_4$ and/or water in the pre-polarization solution causes a much higher initial potential drift of the K-SCISEs (-2.8 mV h^{-1}). However, as a precise tuning of the a_{HQ}/a_{BQ} ratio of the PEDOT-HQ solid contact requires access to protons, the K-SCISEs presented here need still further optimization. Chronopotentiometric measurements reveal more clearly than reported previously for ECPs that only a minor fraction of the very high redox capacitance of the PEDOT-HQ solid contact can be utilized when it is buried beneath the PVC-ISM. This leads us to the conclusion that the PVC-ISMs adapted from the liquid contact ISEs may not necessarily be suitable for SCISEs. We believe that ISMs having higher ion mobilities are more advantageous for obtaining faster ion transfer at the SC/ISM interface. This facilitates the redox conversions of the PEDOT backbone and the HQ pendant groups of the buried SC,

which increases its available redox capacitance. The K-SCISEs presented here were insensitive to light, O₂ and CO₂, but the aqueous layer test reveals the presence of water at the inner electrode interfaces probably because of the hydrophilicity of the HQ pendant groups.

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Scheme and figure captions

Scheme 1. Oxidation and reduction of the PEDOT backbone and the HQ/BQ pendant groups of the PEDOT-HQ film. A⁻ refers to the TFA B⁻ anions.

Figure 1. Cyclic voltammograms of the PEDOT-HQ film recorded in aqueous buffer solutions with (a) pH 0 and (b) pH 5.5 at the scan rates of 5, 10, 20, 50 and 100 mV s⁻¹. RE: Ag/AgCl/3M KCl.

Figure 2. Cyclic voltammograms of (a) the unsubstituted PEDOT film without HQ pendant groups and (b) the PEDOT-HQ film measured in aqueous buffer solution at pH 0 with $v=50$ mV/s. RE: Ag/AgCl/3M KCl.

Figure 3. Light sensitivity of the PEDOT-HQ film measured in 1.0 M KNO₃ at pH 5.5 by exposing it to room light (30 min), darkness (30 min) and intense cold light (30 min; ca. 1.6×10^{-5} lux). Before starting the measurement, the electrode was polarized to its fully oxidized state at 0.55 V in the same electrolyte solution. RE: Ag/AgCl/3 M KCl.

Figure 4. Potential reproducibility (given as SD) of the PEDOT-HQ solid contacts ($n = 5$) measured at the open circuit potential in (a) 0.01 M KTFAB-MeCN and (b) a 9:1 mixture (v/v %) of 0.01 M KTFAB-MeCN and 0.2 M HClO₄, after pre-polarization for 5 min at 0.10, 0.15, 0.20, 0.25 and 0.30 V (vs. Ag/Ag⁺) in the same solutions.

Figure 5. Initial potential stability and reproducibility of the (a) K-SCISE_{org} and (b) K-SCISE_{mix} ($n = 5$) measured in 0.01 M KCl for 24 h. RE: Ag/AgCl/3 M KCl//1.0 M LiOAc.

Figure 6. Potentiometric responses of the (a) K-SCISE_{org} and (b) K-SCISE_{mix} measured in 10^{-9} – 10^{-1} M KCl ($n = 5$). RE: Ag/AgCl/3 M KCl//1.0 M LiOAc.

Figure 7. Potentiometric aqueous layer test performed with the K-SCISE_{mix} ($n = 5$). RE: Ag/AgCl/3 M KCl//1.0 M LiOAc.

Figure 8. Typical potentiometric CO₂ and O₂ sensitivity of the K-SCISEs in a stirred 0.1 M KCl solution. The solution was purged with pure gases in the sequence shown in the figure. RE: Ag/AgCl/3 M KCl//1.0 LiOAc.

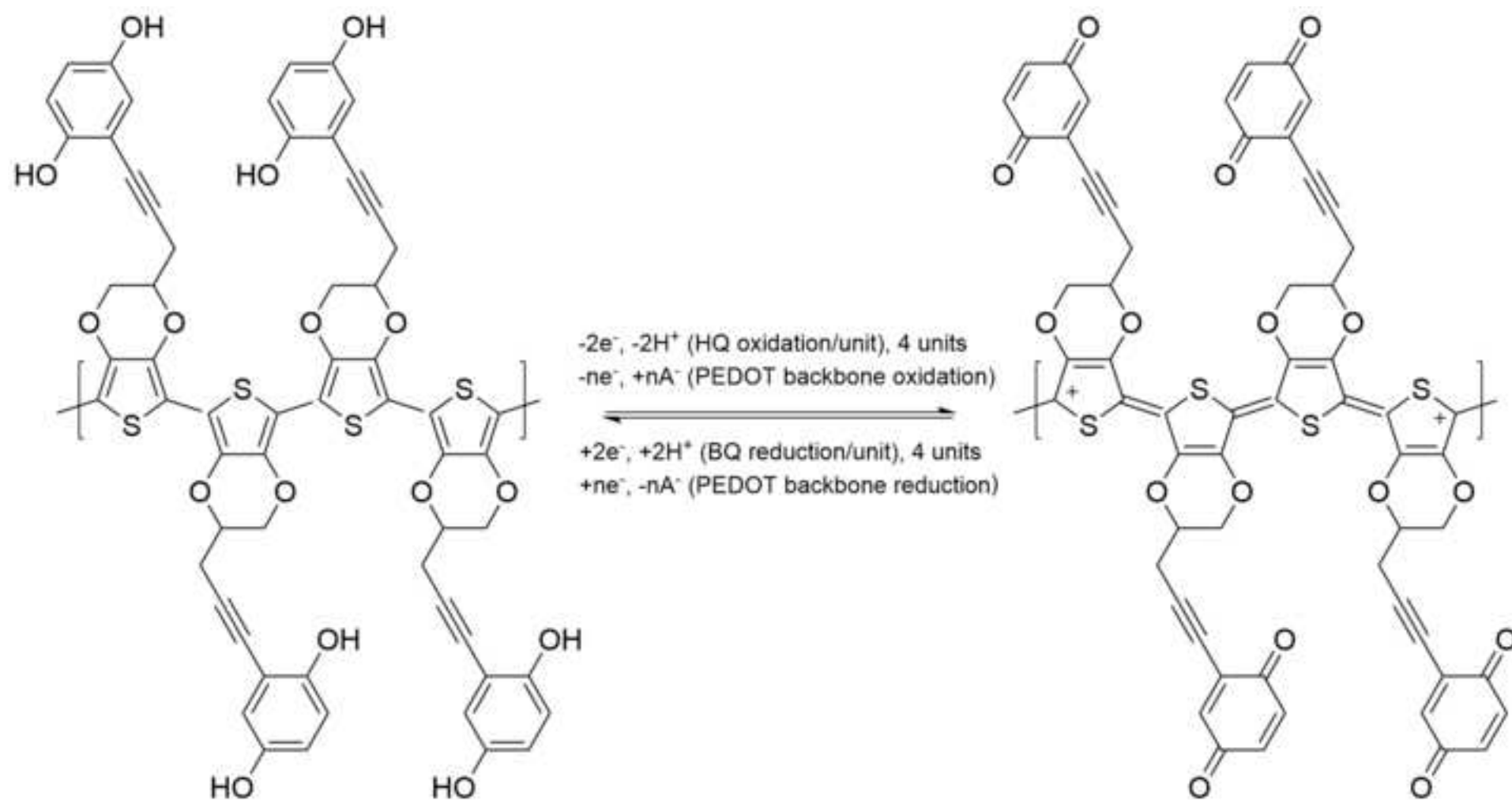
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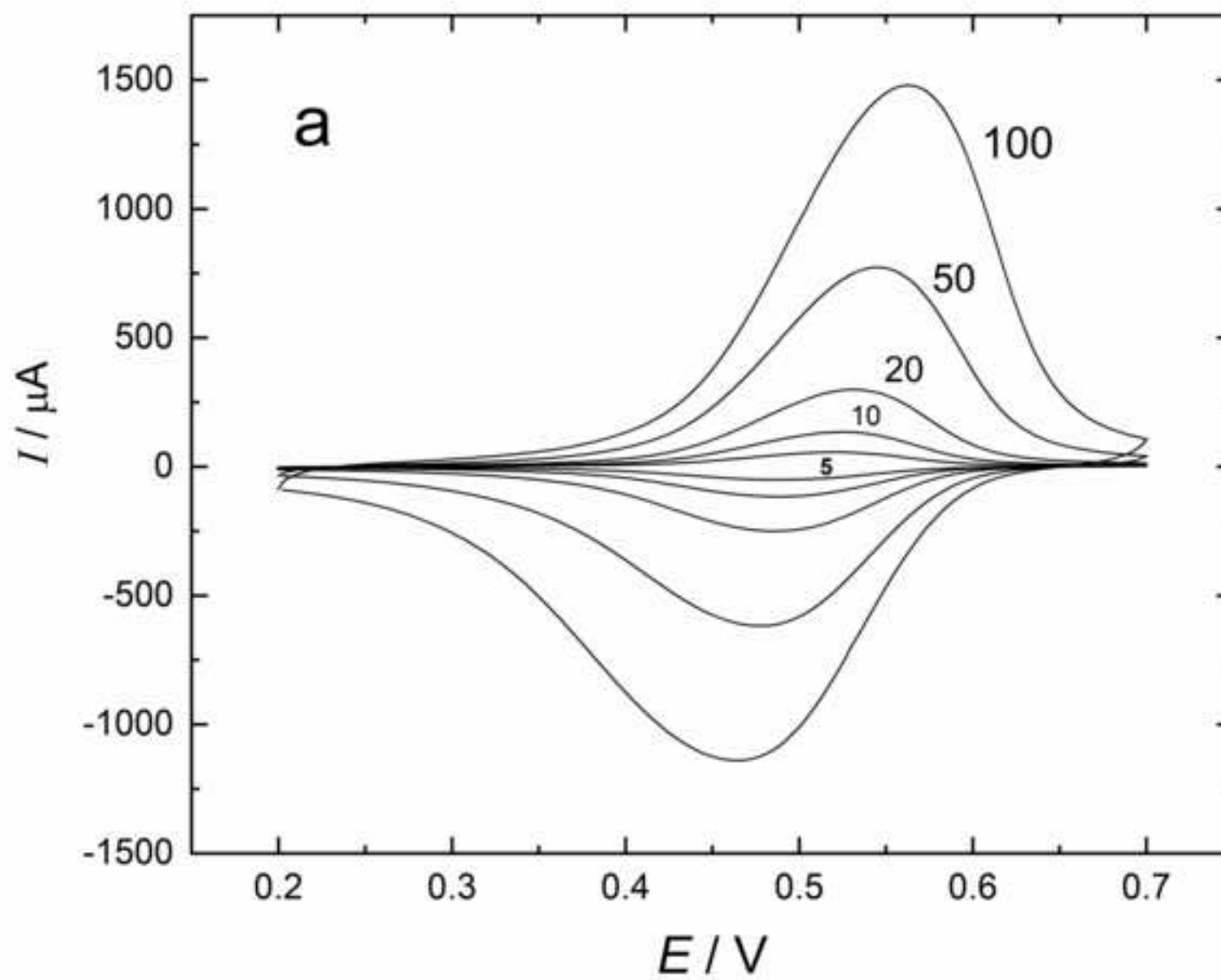
Iryna Ivanko: Investigation, Methodology, Validation, Formal analysis, Visualization, Writing - Original Draft, Writing - Review & Editing, Funding acquisition. **Tom Lindfors:** Conceptualization, Supervision, Methodology, Formal analysis, Visualization, Writing - Original Draft, Writing - Review & Editing, Project administration, Funding acquisition. **Rikard Emanuelsson:** Resources. **Martin Sjödin:** Resources, Writing - Review & Editing.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:





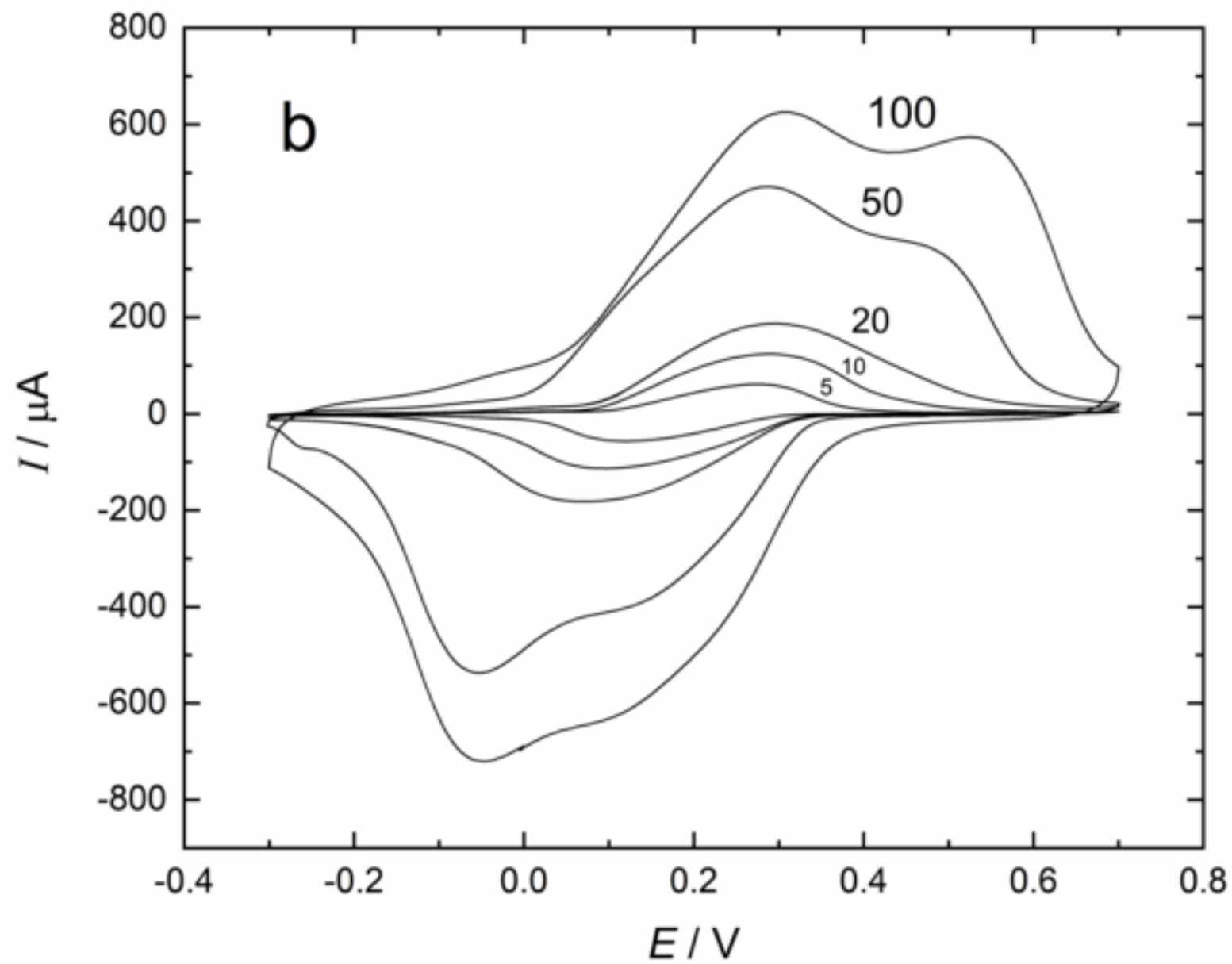


Figure 2

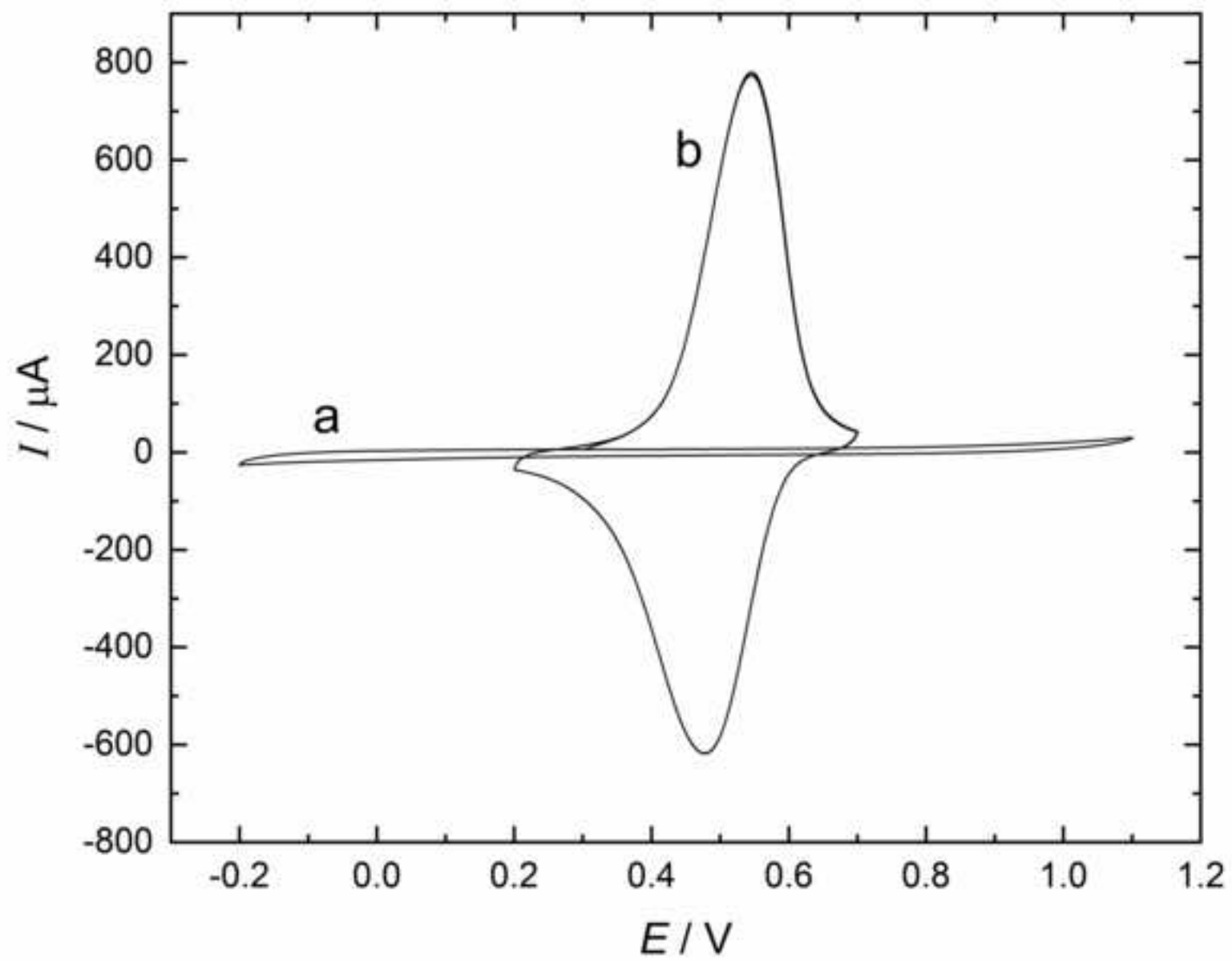


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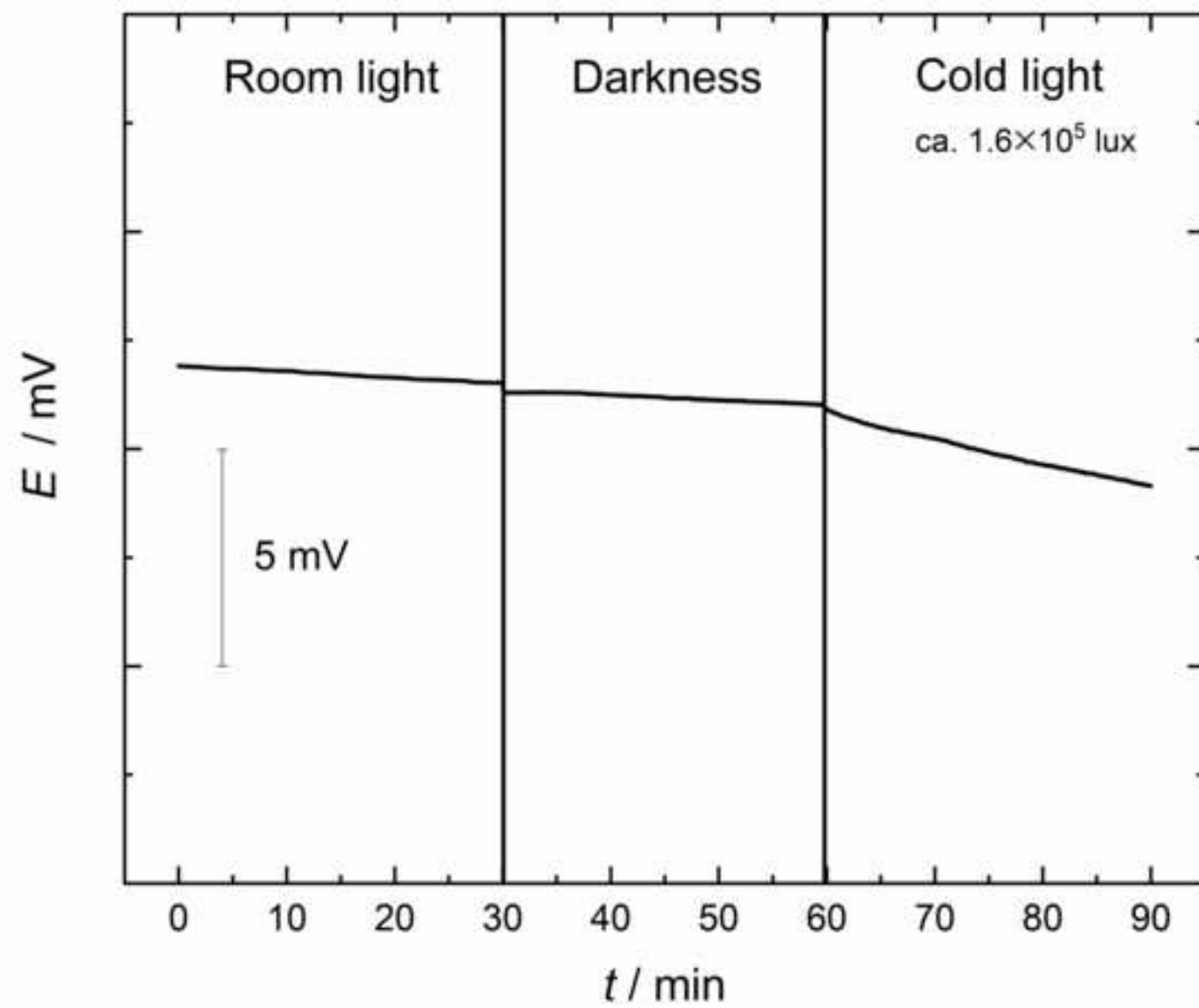


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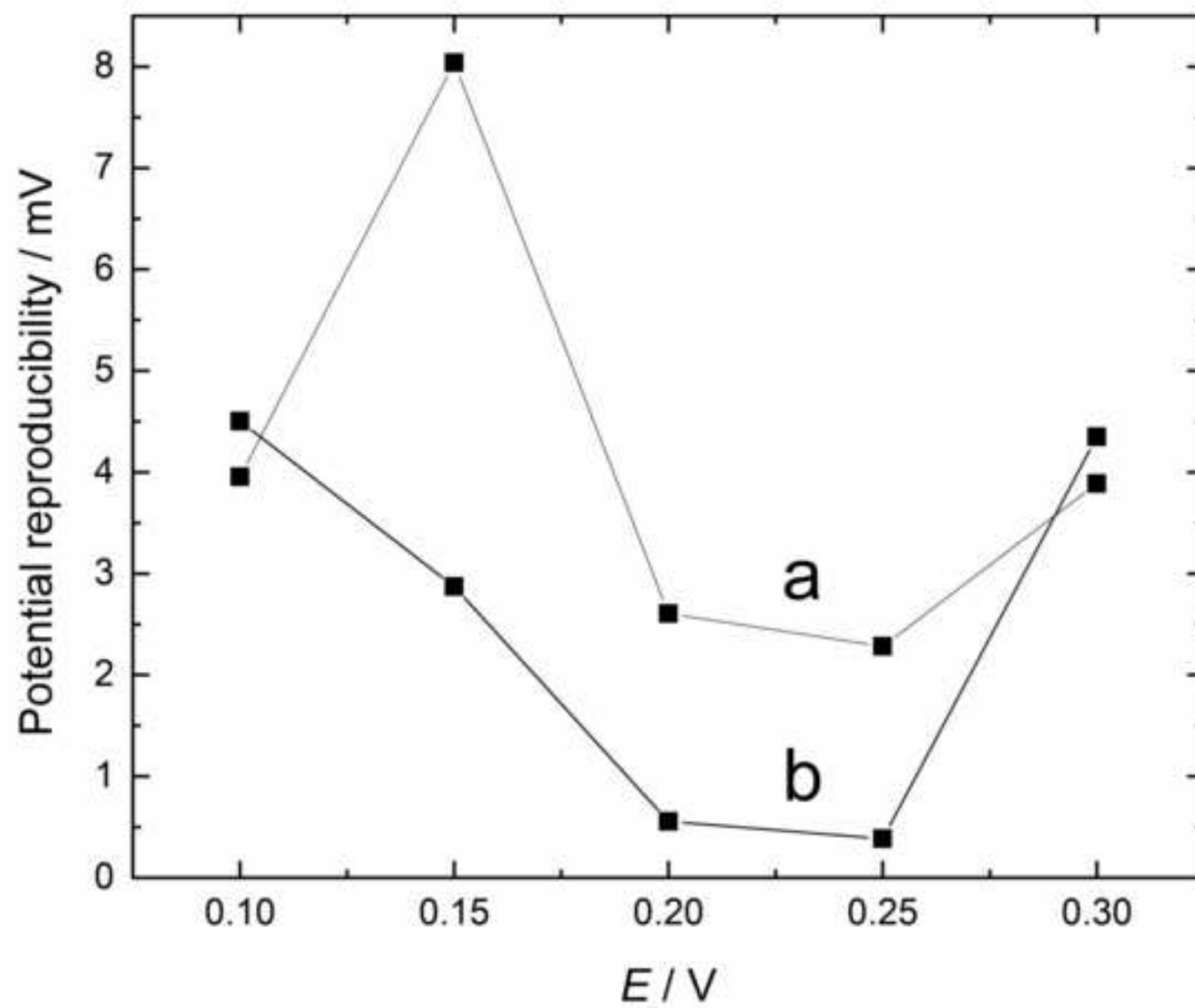


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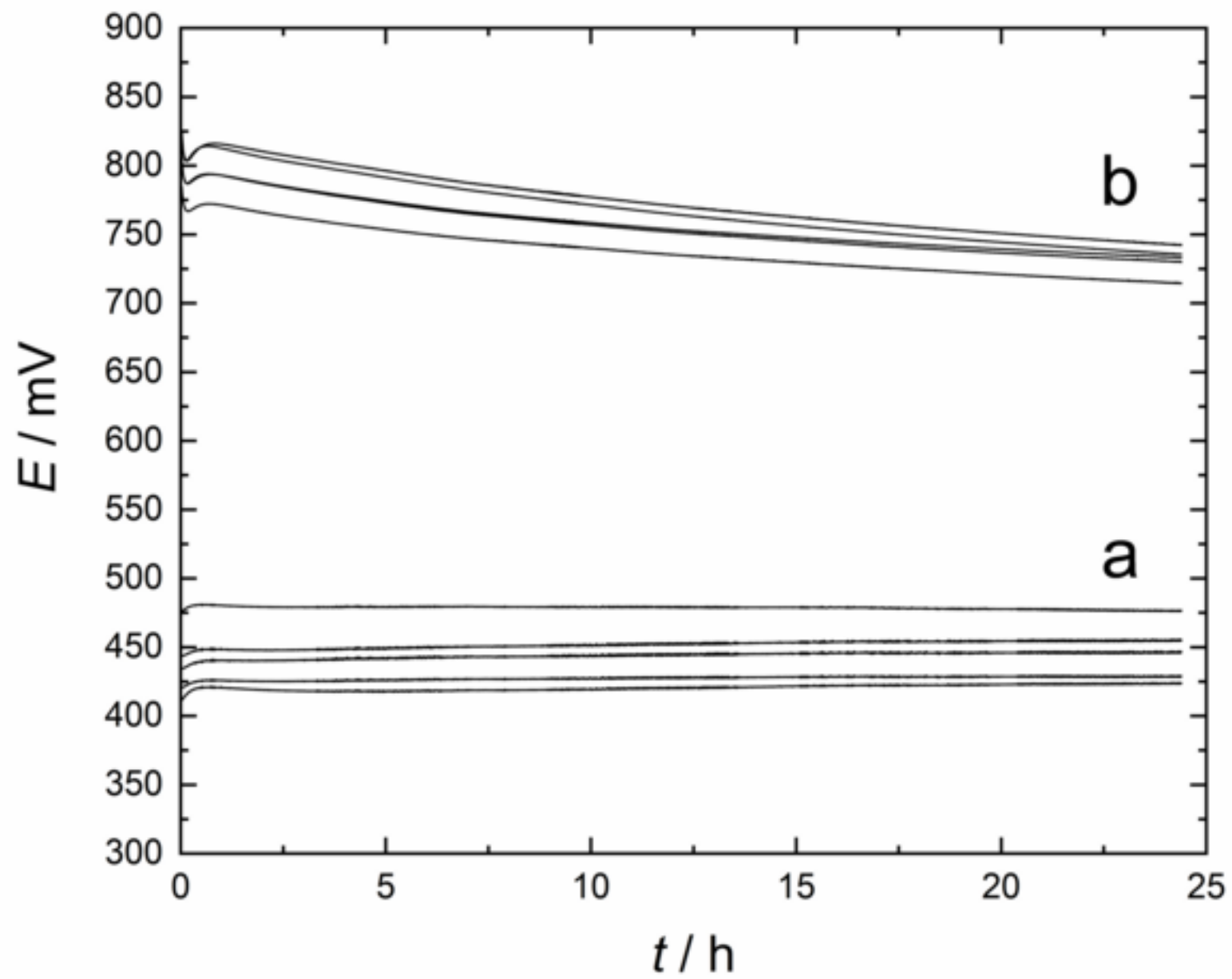


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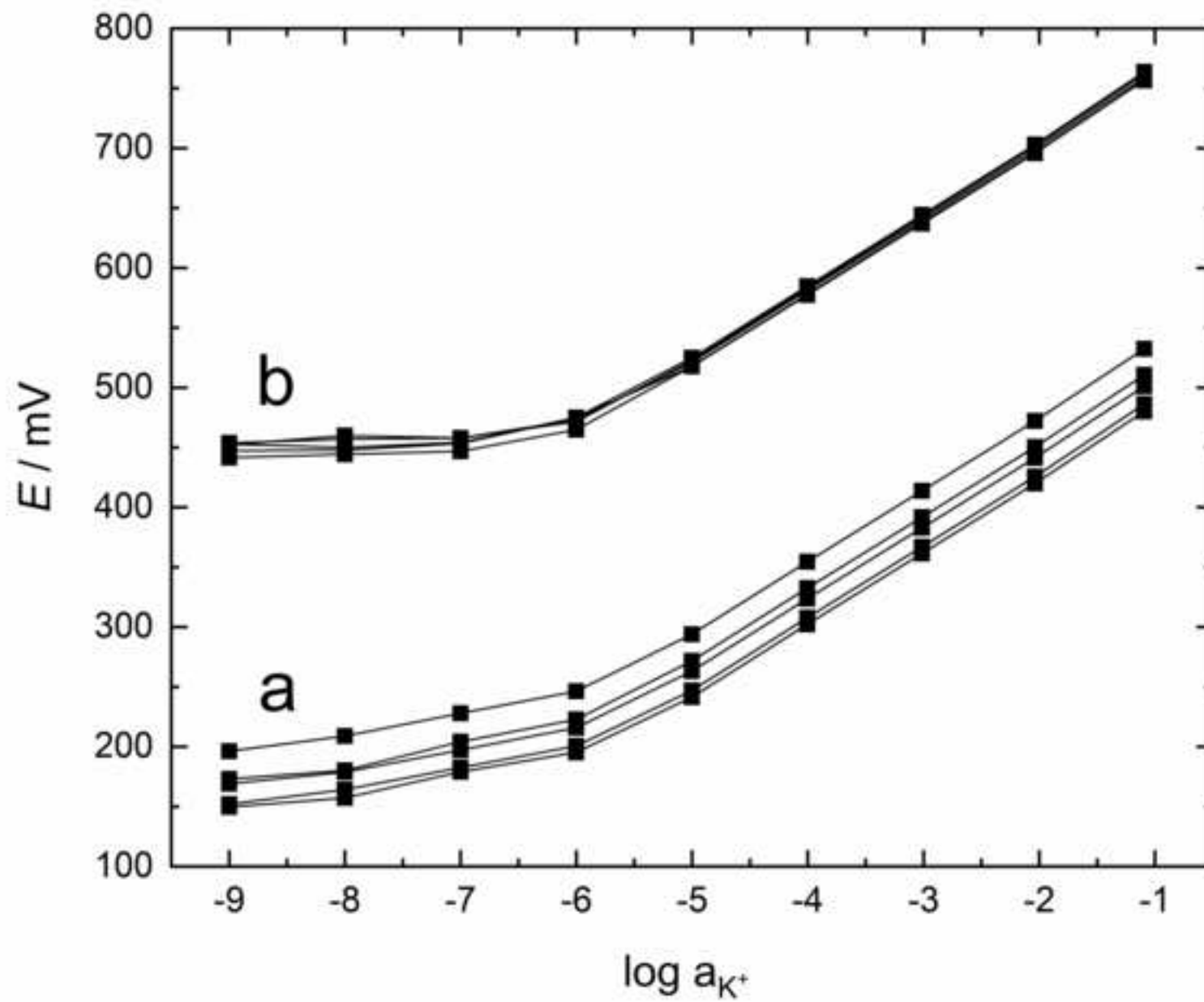


Figure 7

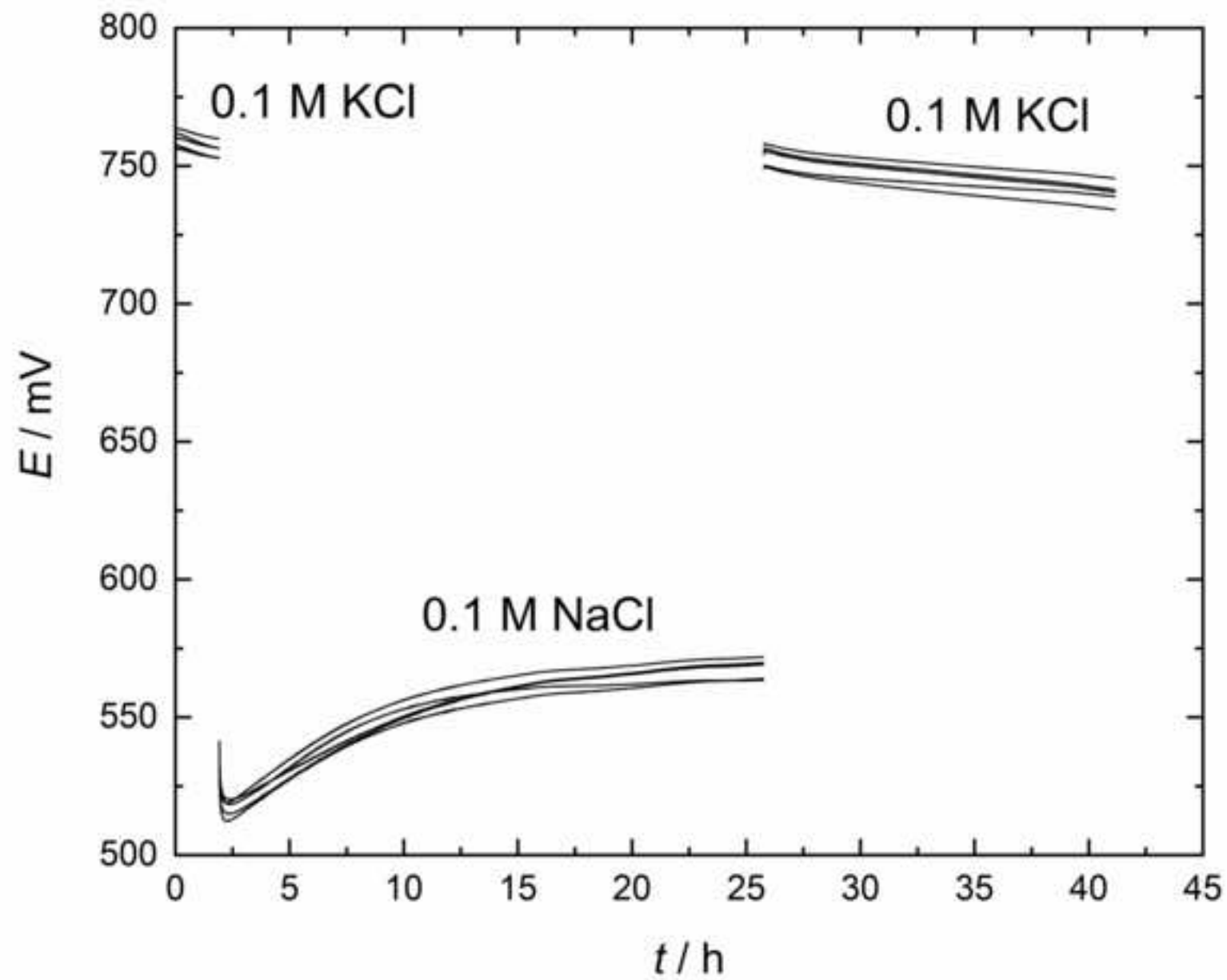
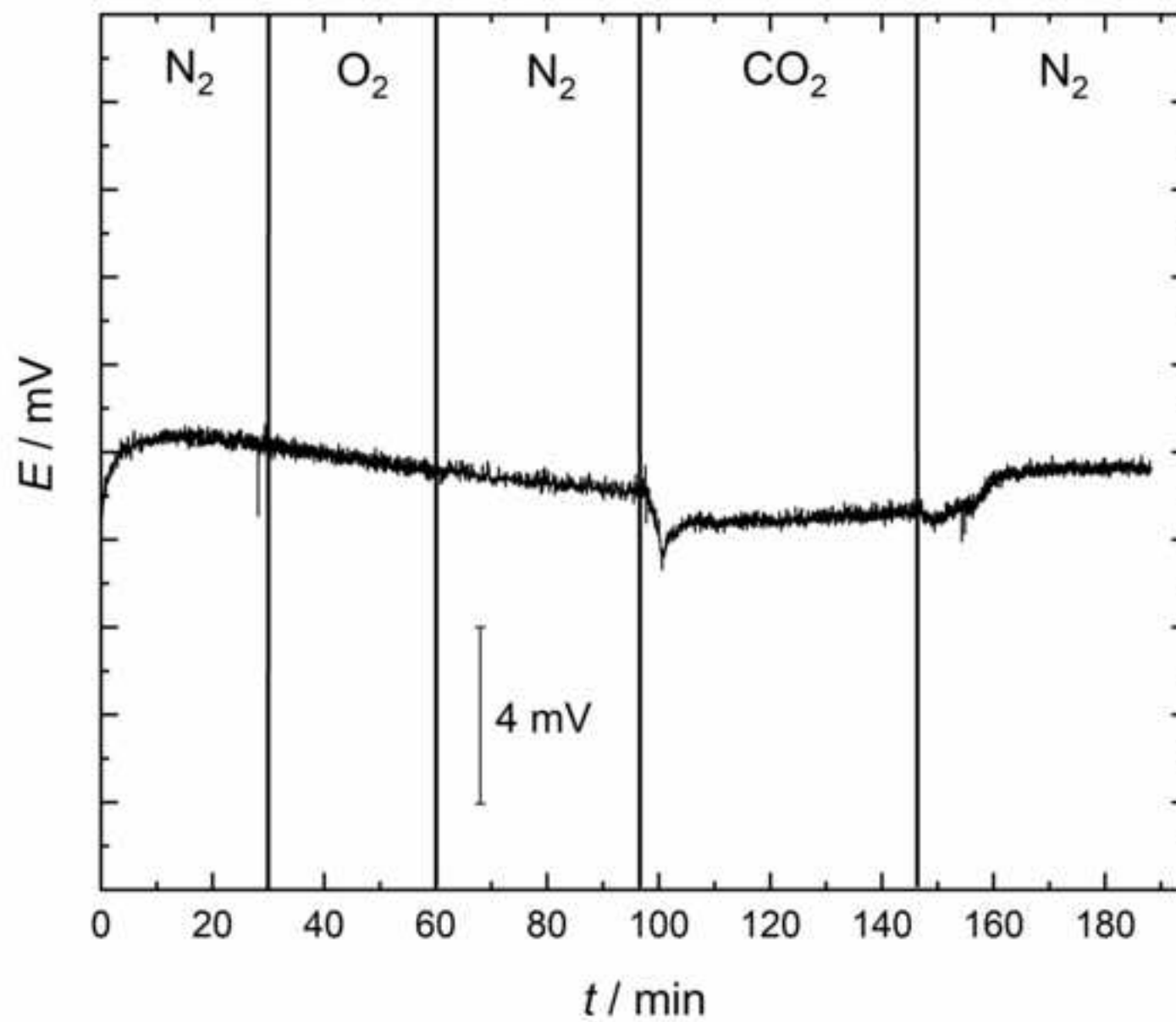


Figure 8



Author biographies

Iryna Ivanko received the MSc degree in Chemistry Sciences from Lviv Ivan Franko University. She is a fourth year PhD student at the Department of Physical and Macromolecular Chemistry at Charles University. Her research focuses on investigation of high-rate pseudosupercapacitors based on semiconducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline. In addition, she is interested in fundamental studies of the photoluminescent properties of individual chains and/or aggregates of PEDOT.

Tom Lindfors is working as Associate Professor in Analytical Chemistry at the Laboratory of Molecular Science and Engineering at Åbo Akademi University (ÅAU). He was in 2004 appointed as Docent in Analytical Applications of Conducting Polymers at ÅAU. His research interests cover solid-state ion-selective electrodes, graphene based composite materials, electrically conducting polymers, water uptake of polymeric ion-selective membrane materials and barrier properties of carbon materials.

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Martin Sjödin is a professor in nanotechnology and functional materials at Uppsala University. He received his Ph. D. degree in Physical Chemistry from Uppsala University in 2004. Between 2004 and 2007 he was a Postdoctoral Fellow, first at Dublin City University (2004-2005) and later at Commissariat à l'Énergie Atomique (Paris) (2005-2007). In 2013, he was appointed Docent in Nanotechnology and Functional Materials and in 2015 he was appointed Full Professor within the same discipline. Currently his research interests are in the area of organic materials for energy conversion and storage.

HIGHLIGHTS

- We have used a conjugated redox polymer (CRP) in ion-selective electrodes
- The CRP was applied for the first time as a solid contact
- It has a PEDOT backbone with covalently bound hydroquinone (HQ) pendant groups
- PEDOT-HQ has superior redox capacitance to unsubstituted PEDOT due to the HQ groups
- The covalent attachment prevents the leaching of the HQ pendant groups