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1 **Ionic liquid redox flow membraneless battery in microfluidic system**

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5 **Abstract**

6 Redox flow batteries (RFBs) often require the presence of a physical membrane to
7 separate the two compartments of the battery. The objective of this work is to develop a
8 membraneless microfluidic redox flow battery (RFB) by using 1-ethyl-3-methylimidazolium
9 bis(trifluoromethylsulfonyl)imide (C₂mimTFSI) as support electrolyte in which Quinone (Q)
10 and iron chloride (FeCl₂) have been used as negolyte (or anolyte) and posolyte (or catholyte),
11 respectively. Polarization curve and cyclic voltammetry were used to characterize the
12 electrochemical properties of the electrochemical systems as well as the performance of the
13 microbattery. The proof-of-concept of the system is presented with an open circuit potential of
14 0.6 V, obtained with both polarization curve and cyclic voltammetry, and with a current density
15 ranging from 0.3 to 0.65 mA.cm⁻² for total flow rates of 10 to 20 μL.min⁻¹. A maximum power
16 of 40 μWcm⁻² has been obtained with this microbattery.

17

18 **Keywords:** C₂mimTFSI, Quinone, FeCl₂, redox flow batteries, membraneless electrochemical
19 cell, microfluidics

20

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21 **1. Introduction**

22 The development of environmentally friendly devices for the storage of renewable
23 energy has become a subject of paramount importance. For instance, the use of less volatile and
24 less toxic chemicals such as ionic liquids (ILs) for a “green chemistry” is a trend that aims to
25 reduce global pollution. These molten salts at room temperature are characterized by their
26 thermal and electrochemical stabilities, a low melting point in comparison with conventional
27 salts (*i.e.*, below 100 °C), a low vapor pressure and wide electrochemical potential windows.
28 Therefore, they have been progressively receiving a lot of interest in various electrochemical
29 applications including electrodeposition, electroplating, electropolishing, and electrolyte for
30 redox flow batteries (RFBs) [1-3].

31 These latter provide direct conversion between chemical and electrical energy and have
32 been widely used as one of the most robust storage systems for renewable energy due to their
33 relatively simple installation and fast response time as well as their wide range of power and
34 energy, suitable for a variety of practical applications. The main advantage of RFBs is their
35 ability to decouple power and energy of the system. In fact, the energy storage capacity depends
36 on both the concentration of the electroactive species dissolved in the electrolyte and the volume
37 of the storage tanks, while the power of the system depends on the number of individual cells
38 and the electroactive surface of the electrodes. These features render RFBs unique, compared
39 to other energy storage systems such as lithium-based batteries, allowing greater flexibility in
40 the individual optimization of power or energy depending on the target application. Despite the
41 fact that almost all aspect RFBs have been studied and that all-vanadium RFBs have been
42 commercialized for various applications including for grid storage, some factors limiting their
43 industrialization on wider scale still exist [4-6]. In particular, many studies have highlighted the
44 need for optimization of the separating membrane, which is a key component of RFB [7-9]. For
45 example, if one thinks solely in terms of cost, the separator membrane alone accounts for more

46 than 10% of the total cost for the vanadium RFBs [10]. In addition, the separator membrane
47 must ensure high proton conductivity, whereas at the same time, the main current issues
48 associated with the use of membrane are numerous, including posolyte and negolyte crossover
49 through the separator, ohmic losses and the swelling and shrinking of the membrane due to the
50 water uptake.

51 Among the various membrane optimization strategies to improve cell performance,
52 membraneless redox flow batteries in microfluidic-based devices are a promising alternative.
53 In these systems, the membrane separator in classical RFBs is eliminated avoiding or improving
54 the aforementioned issues. Since for microfluidic devices, the characteristic dimension of
55 channels is in the order of a hundred of micrometers, it is then relatively simple to achieve a
56 low Reynolds number, resulting in the establishment of co-laminar flows. Therefore, this
57 confined liquid/liquid interface in the microchannel can be considered as a virtual membrane
58 playing the same role than a physical separator membrane. Thanks to the co-laminar regime,
59 the two streams (posolyte and negolyte) containing different electroactive species at different
60 concentrations do not convectively interpenetrate and flow side by side in the microchannel
61 [11-15].

62 The concept of membraneless redox-flow batteries was first reported by Ferrigno *et al.* [16]
63 in 2002, with the development of a millimeter-scale redox fuel cell. The two streams contained
64 the redox couples V^{5+}/V^{4+} and V^{3+}/V^{2+} in 25% H_2SO_4 as posolyte and negolyte, respectively.
65 Carbon-on-gold electrodes were used as current collectors rather than metals to reduce the
66 electrolysis of water as side reactions. This membraneless RFB shows an open circuit voltage
67 of 1.59 V and a maximum current density of 80 mA.cm⁻². More recently, Navalpotro *et al.* [17]
68 reported a membraneless redox flow battery in which vanadium species were replaced by
69 quinone; the two streams being formed by an acidic aqueous solution of hydroquinone (H_2Q)
70 and 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($PYR_{14}TFSI$)

71 containing dissolved parabenzoquinone (pBQ) paving the way to the use of ionic liquids in
72 these batteries. However, in this study, the authors played on the immiscibility of the two
73 electrolytes in such a way as to exclude membrane use. The open circuit voltage and energy
74 density were shown to be 1.4 V and 22.5 WhL⁻¹, respectively. By using different immiscible
75 electrolytes [18] or by changing the redox couple involved in the electrochemical systems [19]
76 both larger operating voltage and power density could have been reached [20]. Interestingly,
77 aqueous membrane-free batteries involving aqueous/aqueous immiscible electrolytes were also
78 investigated showing that in this case, the partition of the electroactive species is a key
79 parameter for these systems working as aqueous biphasic systems (ABS) [21]. However, a large
80 scale membraneless RFB remains a challenge since the mixing of electrolytes is difficult to
81 avoid under dynamic flow conditions [22], whereas the miniaturization of the battery will
82 naturally result in a laminar flow.

83 To the best of our knowledge, and despite the fact that the use of ionic liquids and deep
84 eutectic solvents as electrolytes in RFBs as well as the development of micro-electromechanical
85 systems MEMS-based membraneless RFB have been described in the literature [23-25], the
86 combination of these two components, which should lead to development of high power and
87 membraneless microbatteries, has not yet been reported. In fact, the use of ionic liquids and
88 deep eutectic solvents is beneficial as it allows to obtain a wide electrochemical window as well
89 as a laminar flow in the microchannel thank to their relatively high viscosity compared to the
90 usual electrolytes utilized in RFB. This laminar regime allows to eliminate the separating
91 membrane of the battery.

92 The objective of this work is to develop a membraneless RFB by using 1-ethyl-3-
93 methylimidazolium (bistrifluoromethylsulfonyl)imide (C₂mimTFSI) as support electrolyte and
94 Quinone (Q) and iron chloride (FeCl₂) as electroactive species in a microfluidic system. This
95 IL was selected because of its low viscosity and high conductivity compared to other ILs.

106 Moreover, C₂mimTFSI has a large electrochemical window which seems to be suitable for this
107 application [26]. We first report on the physicochemical properties such as viscosity and
108 electrochemical potential window of the synthesized C₂mimTFSI as well as its electrochemical
109 properties with the two redox mediators. Finally, the proof-of-concept of this new system will
110 be shown with the use of a simple microfluidic device.

101

102 **2. Experimental section**

103 ***2.1. Electrolyte preparation and electrochemical characterizations***

104 The electrolyte consisted of C₂mimTFSI, which was prepared according to the
105 experimental procedure previously described [27], and whose chemical structure is shown in
106 Table 1. The viscosity of the ionic liquid was measured with a rolling-ball viscosimeter (Anton
107 Paar, Lovis 2000M/ME). The ionic conductivity was measured using a Lab CDM 230
108 conductimeter (Radiometer Analytical). The variations in viscosity were studied over a
109 temperature range between 20 to 60°C. The electroactive species quinone (purity \geq 98%) and
110 iron chloride, FeCl₂ (98%) were supplied by Sigma-Aldrich and used as received.

111 The electrochemical characterization of the negolyte and posolyte was performed in a
112 three-electrode cell configuration using a GAMRY REF 600 potentiostat. A gold electrode of
113 100 μ m in radius ($S = 3.14 \cdot 10^{-4} \text{ cm}^2$) was used as the working electrode, a platinum gauze of 1
114 cm² surface area as the counter electrode, and a home-made reference electrode based on Ag/
115 AgNO₃ saturated in IL. However, all the potentials will be reported with respect to the
116 ferrocenemethanol couple (Fc⁺MeOH/FcMeOH) which was used as internal standard for
117 electrochemical measurements.

118

119

120 **2.2. Microfluidic device fabrication and characterization**

121 The microfluidic cell was a Y-type channel and a pair of gold microelectrodes was used
122 as current collectors as sketched in Fig. 1. The millimeter-scale device consists of a main
123 channel (length 30 mm, width 3mm and height 0.5 mm) connected to two inlets and two outlets
124 for handling the electrolytes. The cell in PDMS and gold microelectrodes were fabricated using
125 classical soft lithography and lift-off process. All the details about the device fabrication can be
126 found in previous work [28]. Briefly, microelectrodes consisting of a gold layer of 200 nm and
127 a thin adhesion layer of Cr (10 nm) were deposited in a glass substrate using PECVD process.
128 Microfluidic channel was fabricated by using the conventional molding technique of PDMS,
129 using molds printed either by 3D printer or photolithography fabrication. The gold electrodes
130 were positioned in the middle of the channel with a spacing of 0.5 mm leading to an active
131 electrode area of 0.025 cm². Finally, the channel was covalently bonded to the glass substrate
132 by treating both the PDMS surface and the glass substrate with an oxygen plasma. The precise
133 positioning was performed with the help of marks which were added on the glass substrate, to
134 manually align the microfluidic channel and the electrodes.

135 The supporting electrolytes (C₂mimTFSI) containing the redox mediators were injected
136 into the channel by using a pressure controller (Fluigent MFCS-EZ) offering a precise control
137 of the flow-rates. All experiments were performed using an inverted microscope (Zeiss
138 Axiovert 40 CFL) for observing the laminar flow in the channel. To determine the cell
139 performance, a polarization curve was recorded using a high input impedance voltmeter
140 (Solartron 7055) and pure resistors of different values.

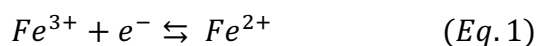
141

142 **3. Results and discussion**

143 **3.1. Electrochemical characterization of the electroactive species in C₂mimTFSI**

144 Table 1 shows three pictures corresponding to the pure ionic liquid (C₂mimTFSI),
 145 quinone (0.35M) in C₂mimTFSI and FeCl₂ (0.1 M) in C₂mimTFSI, respectively. It is worth
 146 noting that these given concentrations represent the maximum concentrations that can be
 147 soluble in the used ionic liquid. All experiments in this work have been performed with these
 148 concentrations. Fig. 2 shows the electrochemical characterization of C₂mimTFSI as electrolyte
 149 in the presence and in the absence of the electroactive species using a gold electrode of 100 μm
 150 in radius. The electrochemical potential window of the ionic liquid was determined using linear
 151 sweep voltammetry (LSV, scan rate 5 mVs⁻¹). As shown in Fig. 2a (black curve), the
 152 electrochemical window of C₂mimTFSI is about 3.5 V which is in agreement with other study
 153 on this ionic liquid [17]. It is noteworthy that this value is much higher than that of aqueous
 154 electrolyte [23] thus enlarging the choice of redox couples to two electrochemical systems with
 155 a higher standard potential difference, thus resulting in higher open circuit potential for the
 156 electrochemical cell.

157 Fig. 2a also shows cyclic voltammograms (CVs) of ferrous ions (0.1 M) in C₂mimTFSI
 158 using gold electrode recorded as a function of the scan rates from 50 mVs⁻¹ to 1 Vs⁻¹. Two
 159 well-defined peaks centered at -0.1 V vs Fc⁺/Fc can be seen and correspond to the one electron
 160 exchange:



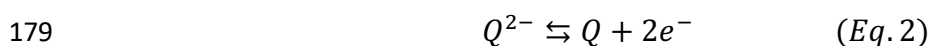
163
 164 The analysis of CV curves allows the determination of Faradaic peak current, I_p , and
 165 peak potential, E_p , as a function of the scan rate, v . When the scan rate is low enough, the
 166 electrochemical system is reversible and the peak intensity is given by [29]:

$$167 \quad I_p = 0.446n^{3/2}FSC^0\sqrt{D}\sqrt{\frac{Fv}{RT}}$$

168 where n is the number of electrons, F is the Faraday constant, S the electrode surface area, C^0
169 the bulk concentration of the electroactive species, R the gas constant, D the diffusion
170 coefficient, and T the absolute temperature (in K).

171 An important feature for a reversible system is the independence of the peak potential
172 as a function of the scan rate. Additionally, the peak width, $E_{p/2} - E_p$, is 56.5 mV and the
173 anodic to cathodic peak potential difference is 57 mV (at 25°C). The slope of the $I_p = f(\sqrt{v})$
174 curve is $2.79 \mu\text{As}^{1/2}\text{V}^{-1/2}\text{cm}^{-2}$, leading to a diffusion coefficient of about $(1.1 \pm$
175 $0.1) 10^{-8} \text{ cm}^2 \text{ s}^{-1}$.

176 Cyclic voltammograms of quinone (0.35 M) in $\text{C}_2\text{mimTFSI}$ as a function of the scan
177 rates are shown in Fig. 3. The two observed peaks refer to the redox reactions of quinone
178 according to Eq. 2:



180
181 Similarly, the current density increases with the scan rates while the oxidation peak
182 increases more quickly than the reduction peak. In addition, the difference between the anodic
183 and cathodic peak potentials is 695 mV at 50 mVs^{-1} and increases to 784 mV at 1000 mVs^{-1}
184 which confirms that this system behaves as a quasi-reversible redox couple in this media. This
185 behavior is contrary to the results in aqueous medium [26] in which a series of organic
186 molecules based on quinone exhibit a reversible kinetics in the same scan rate range.

187
188 In order to determine the open circuit potential expected in a redox cell, cyclic
189 voltammograms of both FeCl_2 (0.1 M) and quinone (0.35 M) at 50 mVs^{-1} are plotted in Fig. 4.
190 A potential difference of 0.64 V is observed.

191

192 **3.2. Performances of membraneless IL-based RFB**

193 **3.2.1. Laminar flow and open circuit potential**

194 The viscosity of the negolyte and posolyte is a key factor in a membraneless RFB since
195 it has a genuine effect in various properties such as the ability to generate co-laminar flows in
196 microchannel, the mass transport rates inside the electrolyte and the required pumping power
197 to ensure a good operation of the RFB. Thus, the viscosity of pure C₂mimTFSI, and of the
198 solutions containing each electroactive species in the IL were measured as a function of
199 temperature ranging from 20 to 60 °C (Fig. 5).

200 At room temperature, the value of the dynamic viscosity of pure C₂mimTFSI is equal
201 to 30.4 mPa.s which is close to the value reported in the literature [30]. As shown in Fig. 5, the
202 viscosities of the three solutions decrease when the temperature increases. Moreover, it is
203 important to note that the addition of electroactive species does not significantly change the
204 viscosity of the electrolyte (less than 5%). This value should be compared to that of pure water
205 at room temperature, 0.9 mPa.s, and that of concentrated sulfuric acid solutions usually used in
206 all vanadium redox flow battery, between 4 and 6 mPa.s, showing that the viscosity value of
207 the ionic liquid is indeed thirty times higher than that of water but only six times that of sulfuric
208 acid usually used in these applications.

209 In order to characterize the flow in the channel, the Reynolds number (R_e) was
210 calculated as

211

212
$$R_e = \frac{\rho v d}{\eta} = \frac{1513.6 * 1.66 * 10^{-4} * 0.5 * 10^{-3}}{31.32 * 10^{-3}} = 0.004$$

213

214 where ρ is the density of the fluid (kg/m^3), v is the flow speed (m/s), d is the characteristic
215 dimension of the channel (m), η is the dynamic viscosity of the fluid ($\text{Pa}\cdot\text{s}$). The obtained value
216 of 0.004 corresponds to a laminar flow in the microfluidic channel.

217 It is interesting to note that the solutions used in this study are differently colored. Thus,
218 the negolyte is dark blue and the posolyte is yellow (as can be seen in Table 1 from the color of
219 the chemicals), which allows a direct visualization of the co-laminar flow in the microchannel
220 and verifying that no interdiffusion of the species occurs during flow. Additionally, in order to
221 check that a co-laminar flow has been well established in the microchannel (Fig. 6a), flow rate
222 ratios of negolyte/posolyte streams can be varied by maintaining the total flow rate constant at
223 a value of $30 \mu\text{L min}^{-1}$. Images of the circulating fluids as well as the measured open circuit
224 potentials are presented in Table 2. Interestingly, the confined liquid/liquid interface between
225 the two streams moves when the flow rates ratio change without any apparent mixing. In
226 particular, a symmetrical flow regime is established between the streams when the same flow
227 rate is applied for each negolyte and posolyte streams (flow rate of $15 \mu\text{L min}^{-1}$). In addition, a
228 zero open circuit potential (E_{oc}) is measured when there is only one electrolyte (negolyte or
229 posolyte) in the main channel (i.e., for flow rates of 30/0 or 0/30, respectively). Then, this open
230 circuit potential value varies as a function of the flow rates to reach an expected value of 0.61
231 V when the flow rate of the two streams is of the same order of magnitude. In conclusion,
232 whatever the flow rate ratios between the two streams, a co-laminar regime is well established
233 in the microfluidic redox-flow battery.

234

235 3.2.2. Polarization curves

236 The experimental set-up of the membraneless RFB shown on Fig. 6a was used to address
237 the polarization curves of the cell, which is the most used technique to characterize the
238 performance of a battery. In order to study the influence of the total flow rate in the main

239 channel on the performance of the cell, two total flow rates of 10 and 20 $\mu\text{L min}^{-1}$, with the
240 same flow rate ratio between negolyte and posolyte streams, were used. The corresponding
241 polarization curves of the cell are shown in Fig. 6b and 6c, respectively.

242 The maximum value of the open circuit potential is about 0.64 V for a total flow rate of
243 10 $\mu\text{L}\cdot\text{min}^{-1}$ (Fig. 6b); this open circuit potential value perfectly agrees with that obtained by
244 cyclic voltammetry and corresponds to thermodynamic value. Two distinct voltage loss regimes
245 can be clearly observed: at low current density, the potential linearly decreases when the current
246 density increases which corresponds to the activation losses and then the ohmic loss regime. It
247 is noteworthy that for both flow rates, no mass transfer region is observed as expected in the
248 polarization curves [31]. This phenomenon can be ascribed to the electrodes geometry, as well
249 described in the literature [32].

250 The maximum power of this battery is obtained for the higher total flow rate (20 μL
251 min^{-1} , Fig. 6c) with a power of 40 $\mu\text{W cm}^{-2}$ for a current density of 0.3 mA cm^{-2} . The power is
252 higher for 20 $\mu\text{L min}^{-1}$ since this flow rate allows a faster replenishment of the depletion layer
253 on planar electrodes than for lower flow rate. Nevertheless, the value of the power remains low
254 due to the fact that the reaction occurs at a planar electrode [32-33]. These results show the
255 possibility of working in a cell without membrane, the use of ionic liquids being beneficial to
256 maintain an interface between two liquids, but also offering the possibility to use other redox
257 couples than vanadium.

258

259 **4. Conclusion**

260 In this work, we showed that the combination of ionic liquids and microfluidics is
261 promising for the development of a membraneless redox-flow microdevice. Thanks to the
262 viscosity of $\text{C}_2\text{mimTFSI}$ and the millimeter-scale of the cell, co-laminar flows were obtained
263 and well controlled at the interface between negolyte and posolyte streams for different flow

264 rate ratios. The proof-of-concept of a membraneless ionic liquid-based redox flow battery has
265 been demonstrated with an open circuit potential of 0.64 V and with a density current ranging
266 from 0.3 to 0.65 mA cm⁻² for total flow rates of 10 to 20 μL min⁻¹ and a maximum of power of
267 40 μW.cm⁻².

268 The low performance of this system compared to others RFBs can be explained by the
269 geometry of the planar electrodes, leading to significant diffusion limitations, and by the low
270 solubility of the electroactive species in ionic liquid. Different strategies can help to enhance
271 the performance of the cell including, for example, the mixture of this ionic liquid with a
272 molecular solvent to increase the electrolyte solubility and the use of 3D porous carbon
273 electrodes due to their large surface area.

274

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Table and Figure captions

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Table 1 Chemical structures and aspect of the compounds used for the preparation of electrolytes.

Table 2 Influence of the flow rate ratio on the laminar flow and the open circuit potential.

Fig. 1 Schematic design of the microfluidic cell.

Fig. 2 (a) CVs performed with an Au electrode (200 μm in diameter) in a 0.1 M FeCl_2 in $\text{C}_2\text{mimTFSI}$ at different scan rates, the black line corresponds to the electrochemical window, (b) variation of the anodic peak current as a function of \sqrt{v} .

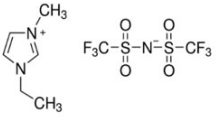
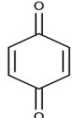




Fig. 3 (a) CVs performed with an Au electrode (200 μm in diameter) in a 0.35 M Quinone in $\text{C}_2\text{mimTFSI}$ at different scan rates, the black line corresponds to the electrochemical window, (b) variation of the anodic peak current as a function of \sqrt{v} .

Fig. 4 CVs performed with a gold electrode (200 μm in diameter) in a 0.1 M FeCl_2 (blue curve) in a 0.35 M Quinone (black curve) in $\text{C}_2\text{mimTFSI}$ at 200 mVs^{-1} .

Fig. 5 Variations of the viscosity of pure $\text{C}_2\text{mimTFSI}$, solution of 0.35 M quinone in $\text{C}_2\text{mimTFSI}$ and solution of 0.1 M FeCl_2 in $\text{C}_2\text{mimTFSI}$ as a function of temperature.

Fig. 6 (a) Experimental set-up and polarization curves of the cell for total flow rate of (b) 10 $\mu\text{L}\cdot\text{min}^{-1}$ and (c) 20 $\mu\text{L}\cdot\text{min}^{-1}$.

412 **Table 1** Chemical structures and aspect of the compounds used for the preparation of
 413 electrolytes.



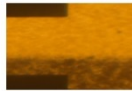
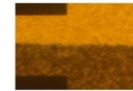
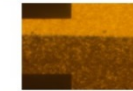
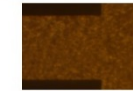
Electrolyte	C ₂ mimTFSI	Quinone (0.35 M) in C ₂ mimTFSI	FeCl ₂ (0.1 M) in C ₂ mimTFSI
Chemical structure			
Aspect			

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416 **Table 2** Influence of the flow rate ratio on the laminar flow and the open circuit potential.

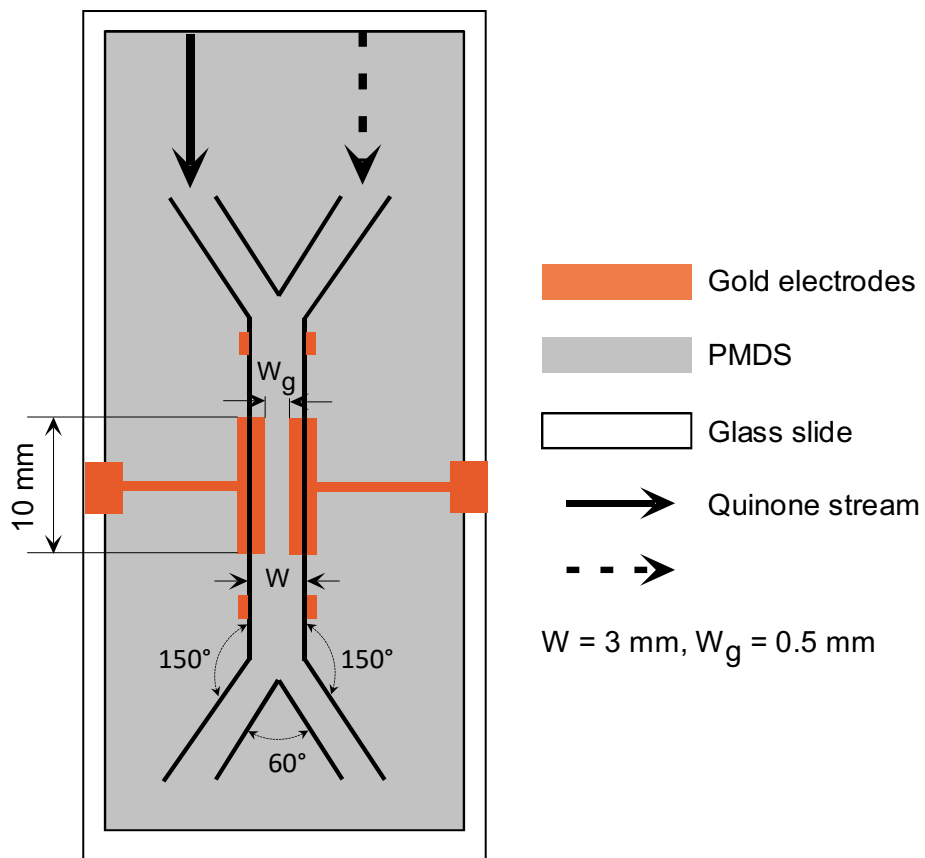
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Flow-rate ($\mu\text{l. min}^{-1}$)	0 – 30	5 – 25	10 – 20	15 – 15	20 – 10	30 – 0
Images						
E_{oc} (V)	0	0.48	0.52	0.61	0.61	0

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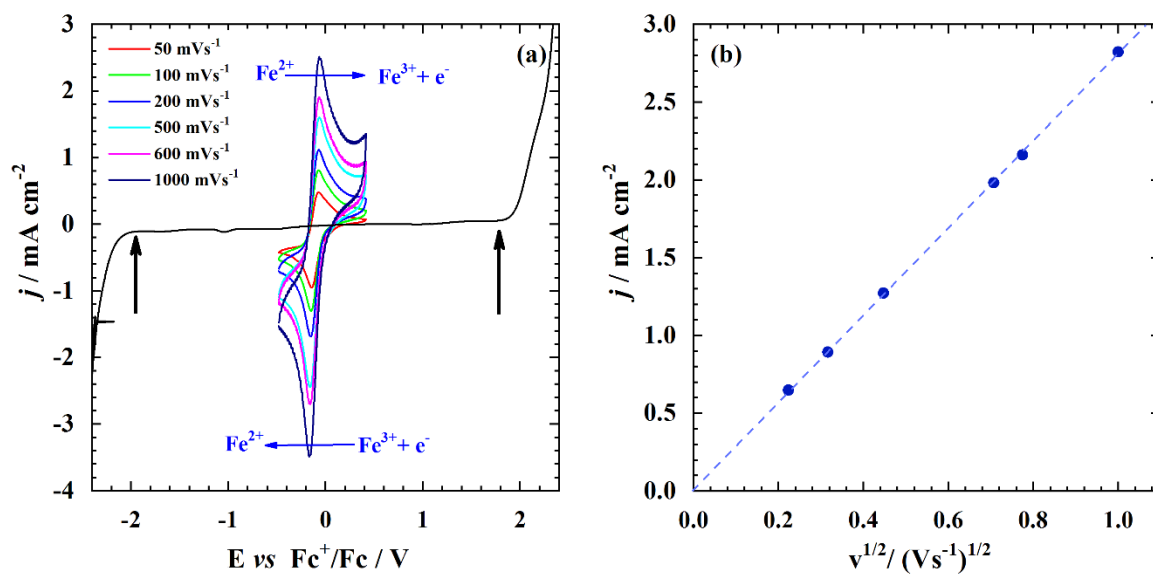
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423 **Fig. 1** Schematic design of the microfluidic cell.

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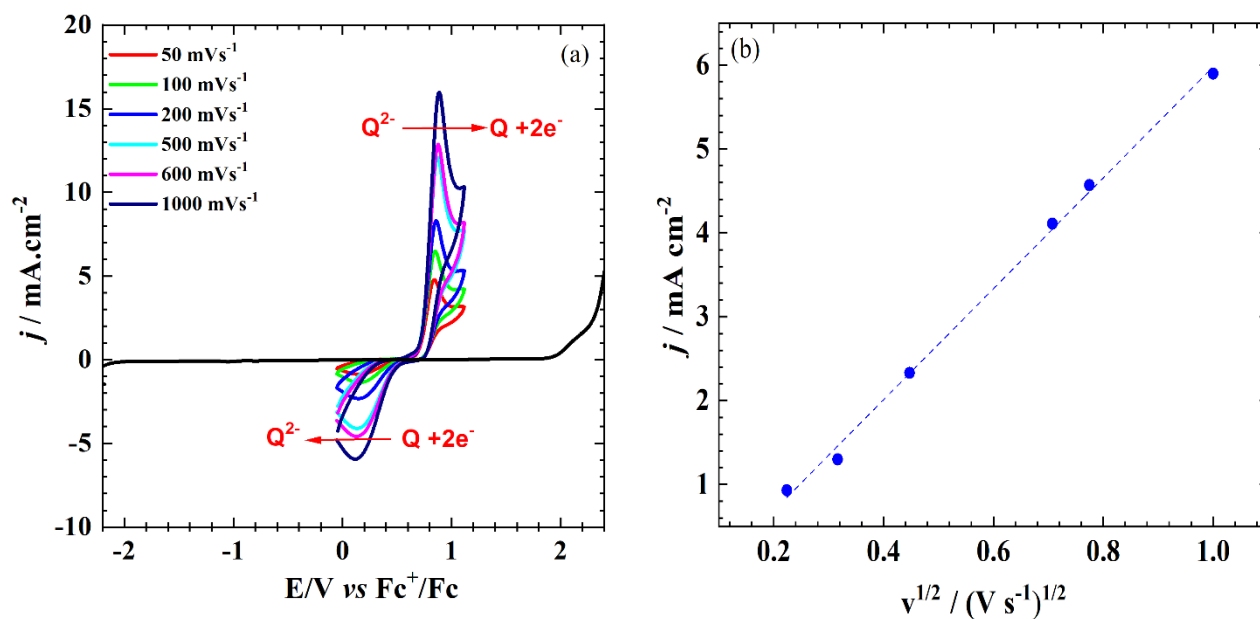
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429 **Fig.2** (a) CVs performed with an Au electrode (200 μm in diameter) in a 0.1 M FeCl_2 in
430 $\text{C}_2\text{mimTFSI}$ at different scan rates, the black line corresponds to the electrochemical
431 window, (b) variation of the anodic peak current as a function of \sqrt{v} .

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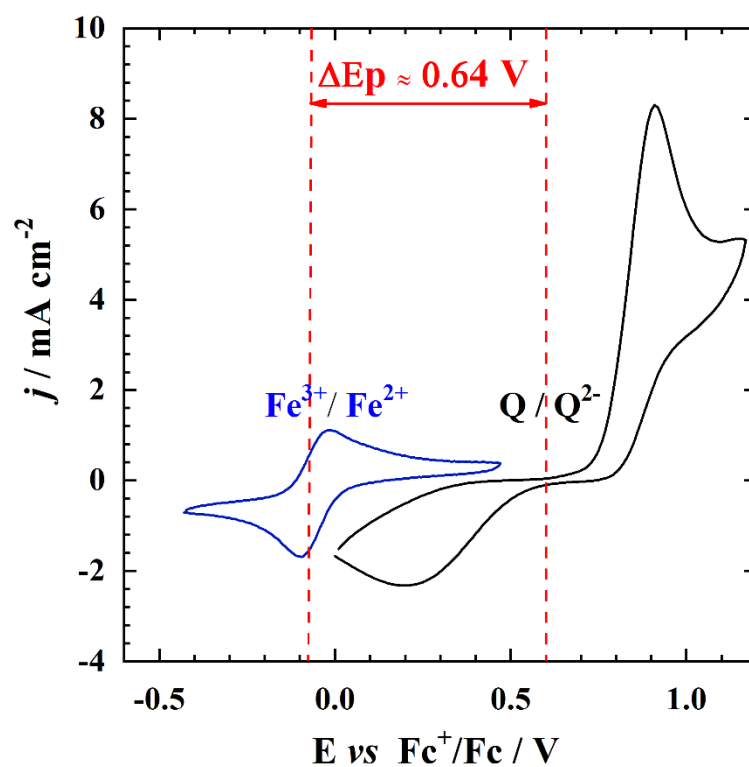
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438 C₂mimTFSI at different scan rates, the black line corresponds to the electrochemical
439 window, (b) variation of the anodic peak current as a function of \sqrt{v} .

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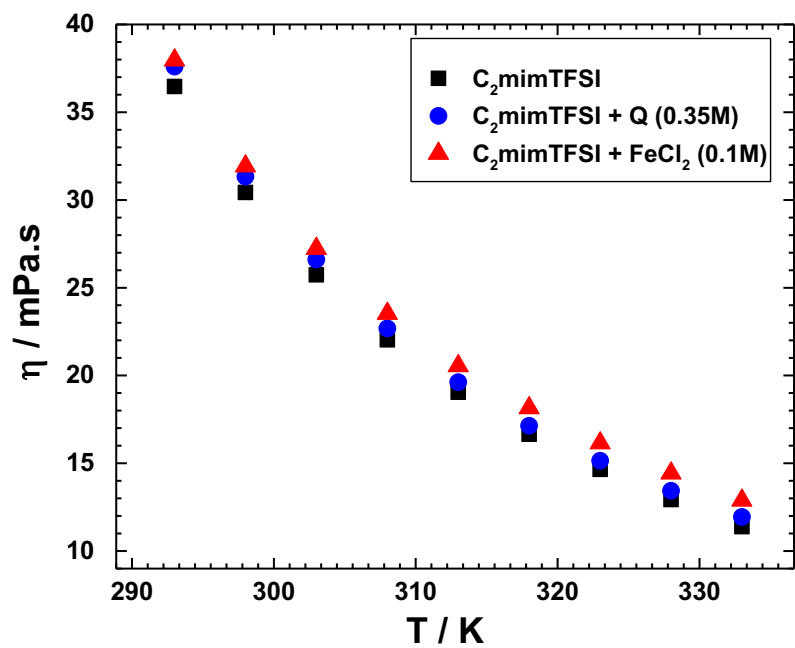


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444 **Fig. 4** CVs performed with a gold electrode (200 μm in diameter) in a 0.1 M FeCl_2 (blue curve)
445 in a 0.35 M Quinone (black curve) in $\text{C}_2\text{mimTFSI}$ at 200 mVs^{-1} .

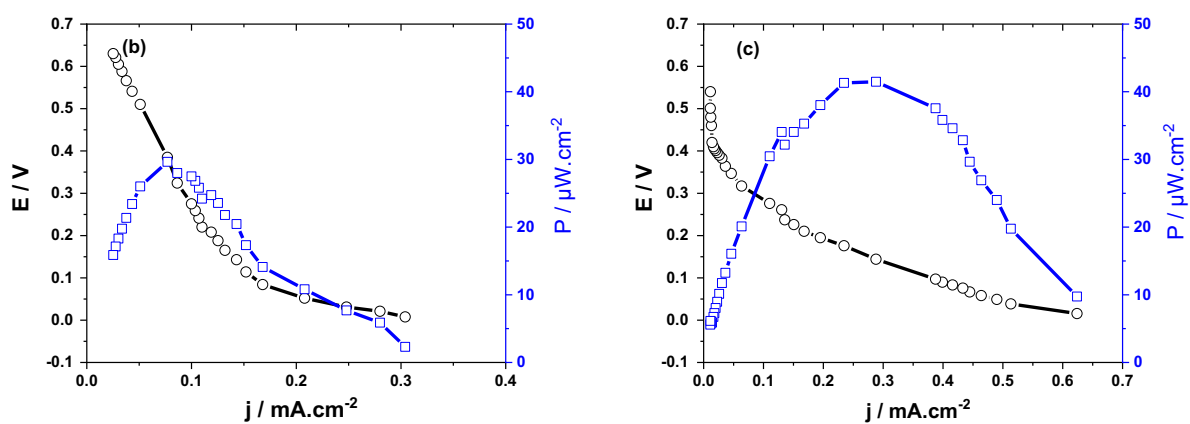
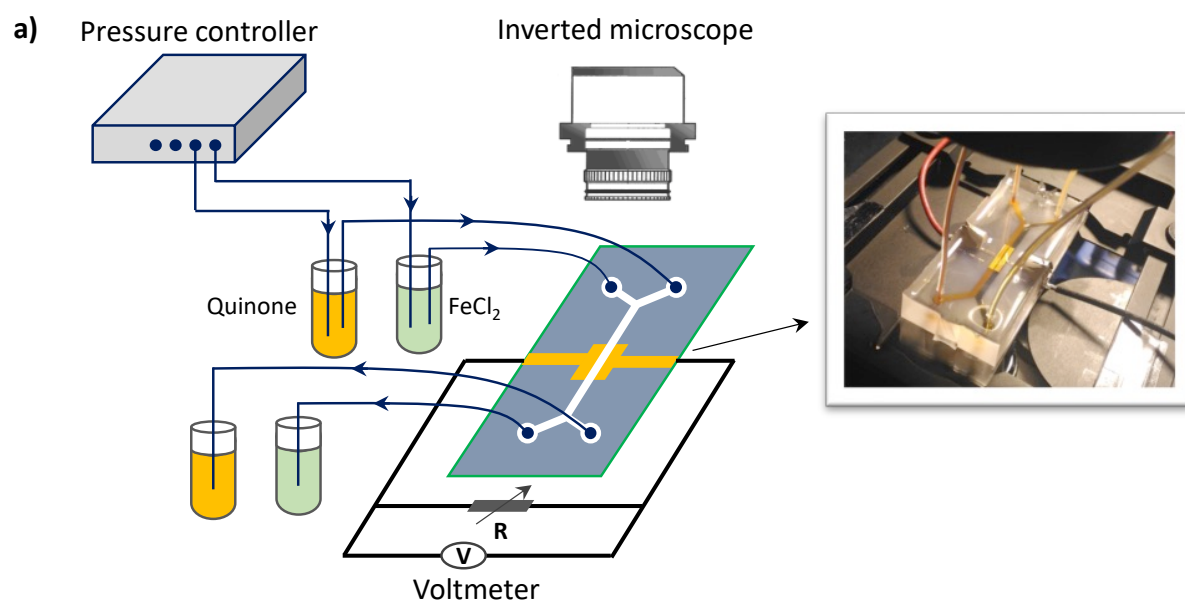
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448 **Fig.5** Variations of the viscosity of pure C₂mimTFSI, solution of 0.35 M quinone in
 449 C₂mimTFSI and solution of 0.1 M FeCl₂ in C₂mimTFSI as a function of temperature.

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453 **Fig. 6** (a) Experimental set-up and polarization curves of the cell for total flow rate of (b) 10
 454 $\mu\text{L} \cdot \text{min}^{-1}$ and (c) $20 \mu\text{L} \cdot \text{min}^{-1}$.

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