

*Supporting information for:*

Scanning Electrochemical Cell Microscopy  
(SECCM) in Aprotic Solvents: Practical  
Considerations and Applications

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## **Table of Contents:**

Section S1. Supplementary experimental section .....	3
Section S2. SECCM probe pulling parameters .....	5
Section S3. Additional experimental data.....	6
Section S4. Movie captions.....	9

## Section S1. Supplementary experimental section

*Chemical reagents and electrode materials.* Propylene carbonate (PC, anhydrous, 99.7%, Sigma-Aldrich, U.K.), dimethyl carbonate (DMC, anhydrous,  $\geq 99\%$ , Sigma-Aldrich), ethylene carbonate (EC, 99+%, Fisher Scientific, U.K.), potassium chloride (KCl, 99.5%, Honeywell, Germany), potassium iodide (KI,  $\geq 99.0\%$ , Sigma-Aldrich), tetra-*n*-butylammonium hexafluorophosphate ( $[\text{NBu}_4][\text{PF}_6]$ ,  $\geq 99.0\%$ , Sigma-Aldrich), lithium perchlorate ( $\text{Li}[\text{ClO}_4]$ , 99.99%, Sigma-Aldrich), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ( $[\text{C}_2\text{mim}][\text{NTf}_2]$ , 99.9%, Solvionic, France), ferrocene (Fc, 98%, Sigma-Aldrich), pyrrole (Py, anhydrous, 99.8%, Sigma-Aldrich) and tetra-*n*-butylammonium iodide ( $[\text{NBu}_4]\text{I}$ ,  $\geq 99\%$ , Sigma-Aldrich) were used as supplied by the manufacturer. All aqueous solutions were prepared with ultrapure deionized water (resistivity =  $18.2 \text{ M}\Omega \cdot \text{cm}$  at  $25^\circ\text{C}$ , Integra HP, Purite, U.K.).

**Table S1.** Physicochemical properties of the solvent (S) and supporting electrolytes (SE): melting point (MP), boiling point (BP), viscosity ( $\eta$ ).

ti	abbreviation	S/SE	MP (°C)	BP (°C)	VP (mmHg) @ 25°C	$\eta$ (cP) @ 25°C
water	N/A	S	0	100	23.8	0.8976
propylene carbonate	PC	S	-49 <sup>[a]</sup>	242 <sup>[a]</sup>	0.045 <sup>[c]</sup>	2.5 <sup>[a]</sup>
dimethyl carbonate	DMC	S	4.6 <sup>[a]</sup>	90 <sup>[a]</sup>	55.4 <sup>[c]</sup>	0.59 <sup>[a]</sup>
ethylene carbonate	EC	S	39 <sup>[a]</sup>	248 <sup>[a]</sup>	$\approx 0.01$ <sup>[c]</sup>	
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	$[\text{C}_2\text{mim}][\text{NTf}_2]$	S/SE	-16 <sup>[b]</sup>			35.55 <sup>[b]</sup>
tetra- <i>n</i> -butylammonium hexafluorophosphate	$[\text{NBu}_4][\text{PF}_6]$	SE	245 <sup>[b]</sup>			
lithium perchlorate	$\text{Li}[\text{ClO}_4]$	SE	236 <sup>[b]</sup>			

<sup>[a]</sup>Taken from Linden, D.; Reddy, T. B. *Handbook of Batteries*, 3rd ed.; McGraw-Hill: New York, 2002.

<sup>[b]</sup>Taken from manufacturer websites

<sup>[c]</sup>Taken from Daubert TE, Danner RP; *Physical and Thermodynamic Properties of Pure Chemicals Data Compilation*. Taylor and Francis: Washington, D.C., 1996

The nanocrystalline Au working electrode (WE) was prepared by evaporating a 2 nm Cr adhesion layer followed by a 75 nm Au layer on an oxidized Si ( $\text{SiO}_2$ ) wafer. The polycrystalline Pt WE was prepared by hand polishing Pt foil to a mirror finish (with subsequently, 30, 9, 3, 1 and 0.25 and 0.05  $\mu\text{m}$  diamond suspensions on a MicroCloth, all from Buehler, U.S.A.) and flame annealing in a butane flame, prior to use. The Ag/AgCl quasi-

reference counter electrode (QRCE) was prepared by anodizing an Ag wire (0.25 mm diameter, 99.99%, Goodfellow, U.K.) in an aqueous saturated KCl solution. The Ag/AgI QRCE was prepared in a likewise fashion in aqueous saturated KI solution. The stable QRCE reference potentials were calibrated against the IUPAC recommended ferrocene/ferrocenium ( $\text{Fc}^{0/+}$ ) process in the pertinent solutions, as summarized in Table S1.

**Table S2.** Reference potentials of the Ag/AgCl and Ag/AgI QRCEs vs the  $\text{Fc}^{0/+}$  process.

QRCE	Solution	$E$ (V) vs $\text{Fc}^{0/+}$
Ag/AgCl	PC / 0.1 M $[\text{NBu}_4][\text{PF}_6]$	-0.41
Ag/AgI	PC / 0.005 M $[\text{NBu}_4]\text{I}$ + 0.1 M $[\text{NBu}_4][\text{PF}_6]$	-0.82

*Surface characterization.* Optical microscopy (OM) images were obtained on a BH2 optical microscope (Olympus, Japan). Scanning electron microscopy (SEM) imaging of the probe tips (Figure 1b) or WE surfaces (*vide infra*) was carried out on a GeminiSEM 500 system (Zeiss, Germany). Electron backscattered diffraction (EBSD) on the polycrystalline Pt working electrode surface was carried out on a JSM-7800F FEG-SEM (JEOL, Japan) at an acceleration voltage of 20 keV, with the sample tilted  $70^\circ$  to the detector. The EBSD data were processed using HKL CHANNEL5 software (Tango, Oxford Instruments, U.K.) to extract inverse pole figure (IPF) and misorientation coloring images/maps.

*Data processing and analysis.* After acquisition, the raw electrochemical data were processed using the Matlab R2018b (9.5.0.944444, Mathworks, U.S.A.) software package. Sample tilt/z-piezoelectric positioner drift in the topographical maps was corrected using the scanning probe image processing software package (SPIP v. 6.0.14, Image Metrology, Denmark). Data plotting was carried out using the Matlab R2018b (movies and maps) and OriginPro 2019 64bit (9.6.0.172, OriginLab, U.S.A.) software packages. Note that all electrochemical/topographical images are presented without any data interpolation.

## **Section S2. SECCM probe pulling parameters**

### **Probes of *ca.* 200 nm diameter (main text, Figure 1b-i):**

Line 1: HEAT 350, FIL 3, VEL 40, DEL 220, PUL 0

Line 2: HEAT 350, FIL 3, VEL 40, DEL 180, PUL 100

### **Probes of *ca.* 750 nm diameter (main text, Figure 1b-ii):**

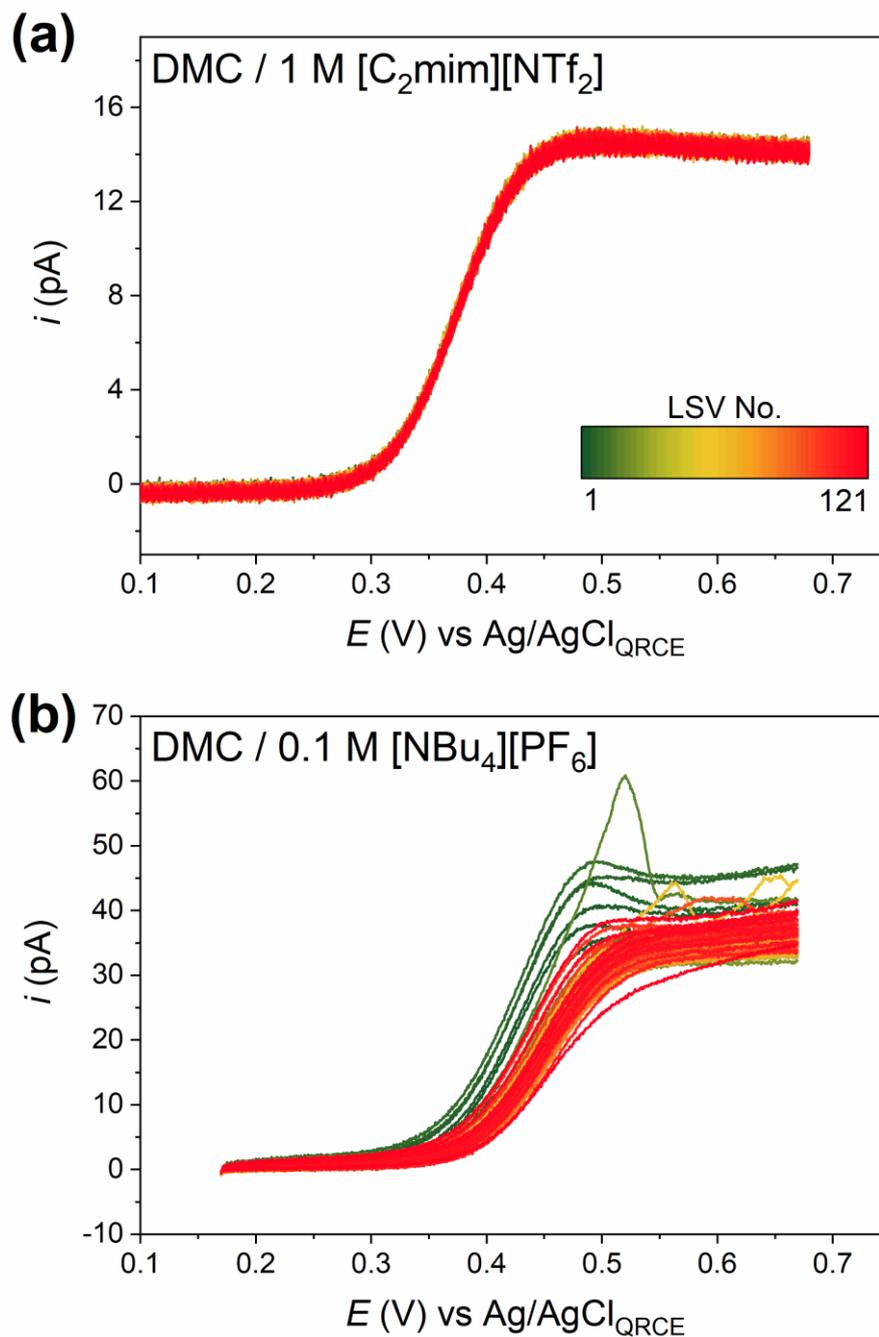
Line 1: HEAT 350, FIL 3, VEL 30, DEL 220, PUL 0

Line 2: HEAT 350, FIL 3, VEL 40, DEL 180, PUL 120

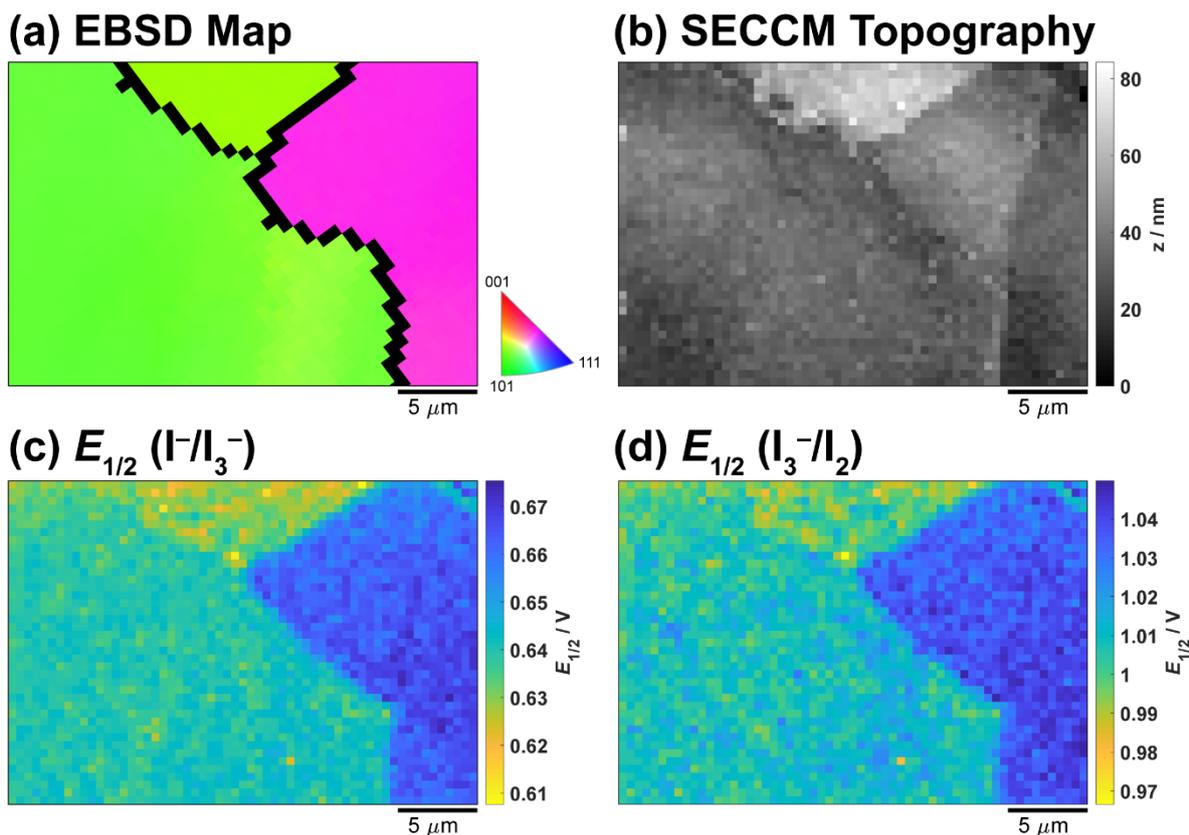
### **Probes of *ca.* 1.7 $\mu\text{m}$ diameter (main text, Figure 1b-iii):**

Line 1: HEAT 350, FIL 4, VEL 40, DEL 200, PUL 0

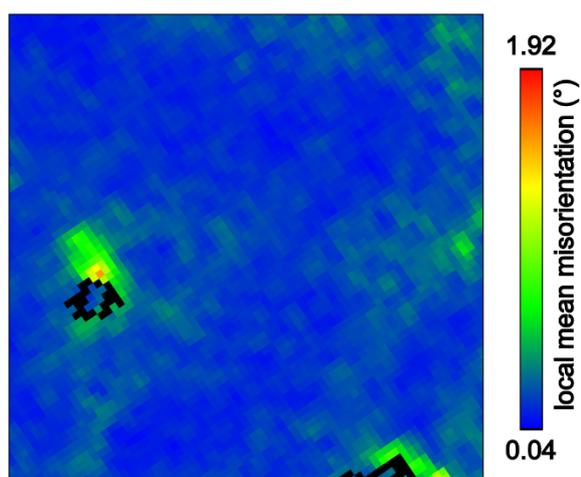
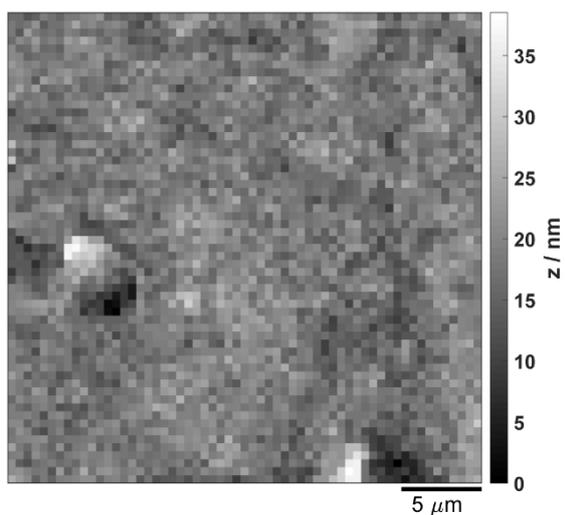
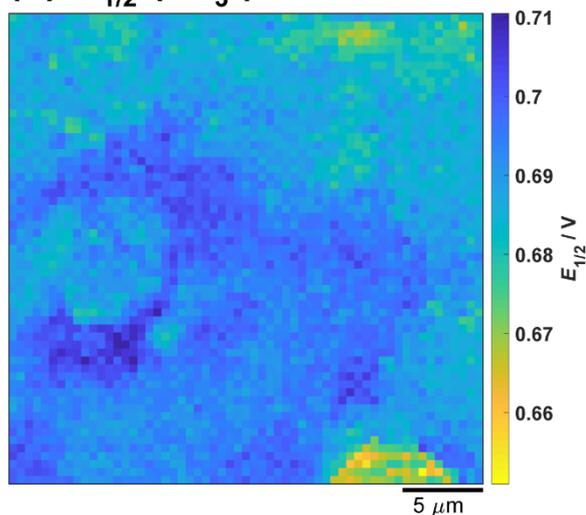
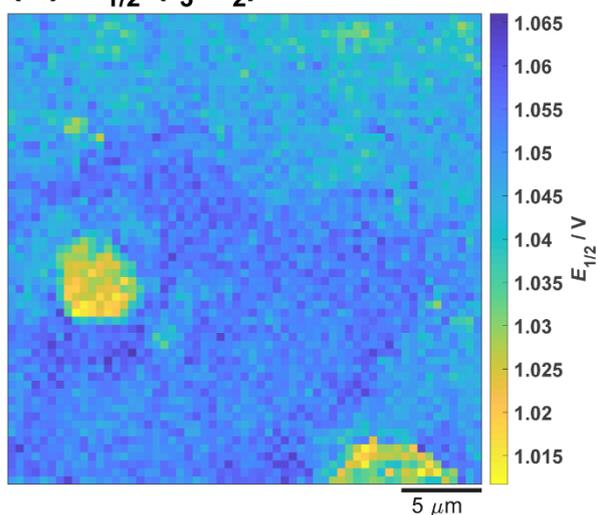
### Section S3. Additional experimental data



**Figure S1.** 121 independent linear-sweep voltammograms (LSVs) obtained from the oxidation of 5 mM Fc at a nanocrystalline Au electrode in (a) DMC (1 M [C<sub>2</sub>mim][NTf<sub>2</sub>]) and (b) DMC (0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>]). The LSVs were obtained in the SECCM configuration with  $d_t \approx 750$  nm (main text, Figure 1b-ii) and voltammetric scan rate ( $v$ ) = 0.5 V s<sup>-1</sup>.



**Figure S2.** (a) EBSD map of a polycrystalline Pt surface, scanned with SECCM (IPF-z indicates surface crystallographic orientation). SECCM (b) topography, (c)  $E_{1/2}$  ( $I^-/I_3^-$ ) and (d)  $E_{1/2}$  ( $I_3^-/I_2$ ) maps ( $59 \times 41$  pixels<sup>2</sup> over a  $29.5 \times 20.5 \mu\text{m}^2$  area, hopping distance = 500 nm). (c) and (d) were constructed from the  $i$ - $E$  data shown in the Supporting Information, Movie S2. (b – d) were obtained in the SECCM configuration ( $d_t \approx 200$  nm, main text, Figure 1b-i) in a 5 mM  $[\text{NBu}_4]\text{I}$  in PC (0.1 M  $[\text{NBu}_4][\text{PF}_6]$ ) solution.

**(a) Misorientation Map****(b) SECCM Topography****(c)  $E_{1/2} (\Gamma^-/I_3^-)$** **(d)  $E_{1/2} (I_3^-/I_2)$** 

**Figure S3.** (a) EBSD misorientation map of a polycrystalline Pt surface, scanned with SECCM. SECCM (b) topography, (c)  $E_{1/2} (\Gamma^-/I_3^-)$  and (d)  $E_{1/2} (I_3^-/I_2)$  maps ( $59 \times 59$  pixels<sup>2</sup> over a  $29.5 \times 29.5$   $\mu\text{m}^2$  area, hopping distance = 500 nm). (c) and (d) were constructed from the  $i$ - $E$  data shown in the Supporting Information, Movie S3. (b – d) were obtained in the SECCM configuration ( $d_t \approx 200$  nm, main text, Figure 1b-i) in a 5 mM [NBu<sub>4</sub>]I in PC (0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>]) solution.

## Section S4. Movie captions

**Movie S1.** Spatially-resolved electrochemical ( $i-E$ ) movie (3481 pixels over a  $29.5 \times 29.5 \mu\text{m}^2$  scan area, hopping distance = 500 nm) obtained with the voltammetric ( $v = 1 \text{ V s}^{-1}$ ) hopping mode SECCM protocol, visualizing the  $\Gamma/\text{I}_3^-$  and  $\text{I}_3^-/\text{I}_2$  processes on a polycrystalline Pt surface. The nanopipet probe (diameter,  $d \approx 200 \text{ nm}$ , image shown in the main text, Figure 1a-i) contained 5 mM  $[\text{NBu}_4]\text{I}$  in PC (0.1 M  $[\text{NBu}_4][\text{PF}_6]$ ) solution. The co-located EBSD map is shown in the main text, Figure 5. The data presented are not interpolated.

**Movie S2.** Spatially-resolved electrochemical ( $i-E$ ) movie (2419 pixels over a  $29.5 \times 20.5 \mu\text{m}^2$  scan area, hopping distance = 500 nm) obtained with the voltammetric ( $v = 1 \text{ V s}^{-1}$ ) hopping mode SECCM protocol, visualizing the  $\Gamma/\text{I}_3^-$  and  $\text{I}_3^-/\text{I}_2$  processes on a polycrystalline Pt surface. The nanopipet probe (diameter,  $d \approx 200 \text{ nm}$ , image shown in the main text, Figure 1a-i) contained 5 mM  $[\text{NBu}_4]\text{I}$  in PC (0.1 M  $[\text{NBu}_4][\text{PF}_6]$ ) solution. The co-located EBSD map is shown in the Supporting Information, Figure S2. The data presented are not interpolated.

**Movie S3.** Spatially-resolved electrochemical ( $i-E$ ) movie (3481 pixels over a  $29.5 \times 29.5 \mu\text{m}^2$  scan area, hopping distance = 500 nm) obtained with the voltammetric ( $v = 1 \text{ V s}^{-1}$ ) hopping mode SECCM protocol, visualizing the  $\Gamma/\text{I}_3^-$  and  $\text{I}_3^-/\text{I}_2$  processes on a polycrystalline Pt surface. The nanopipet probe (diameter,  $d \approx 200 \text{ nm}$ , image shown in the main text, Figure 1a-i) contained 5 mM  $[\text{NBu}_4]\text{I}$  in PC (0.1 M  $[\text{NBu}_4][\text{PF}_6]$ ) solution. The co-located EBSD map is shown in the main text, Figure 6. The data presented are not interpolated.