

Electrochemical investigation of covalently post-synthetic modified SURGEL coatings

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ESI 1. Experimental section.

Chemicals: 2,2'-diazido-4,4'-stilbenedicarboxylic acid (DA-SBDC) and the cross-linker trimethylolethane tripropiolate were synthesized as described in the literature.¹ All the solvents, the catalysts as well as the 6(ferrocene)thiol are commercial available and were used just as purchased. **Substrates for SURMOF growth:** As substrate Si(100) wafers coated with 5 nm Ti and 100 nm Au were used. The substrates were obtained by Georg-Albert-PVD, Germany. **SURMOF growth, cross-linking reaction and EDTA treatment** were performed as described in the literature.¹ For the current study 10 layers of SURMOF were prepared using the spray method followed by crosslinking in toluene for 5 days at 80 C. Figure ESI1 illustrates the schematic SURGEL preparation procedure.

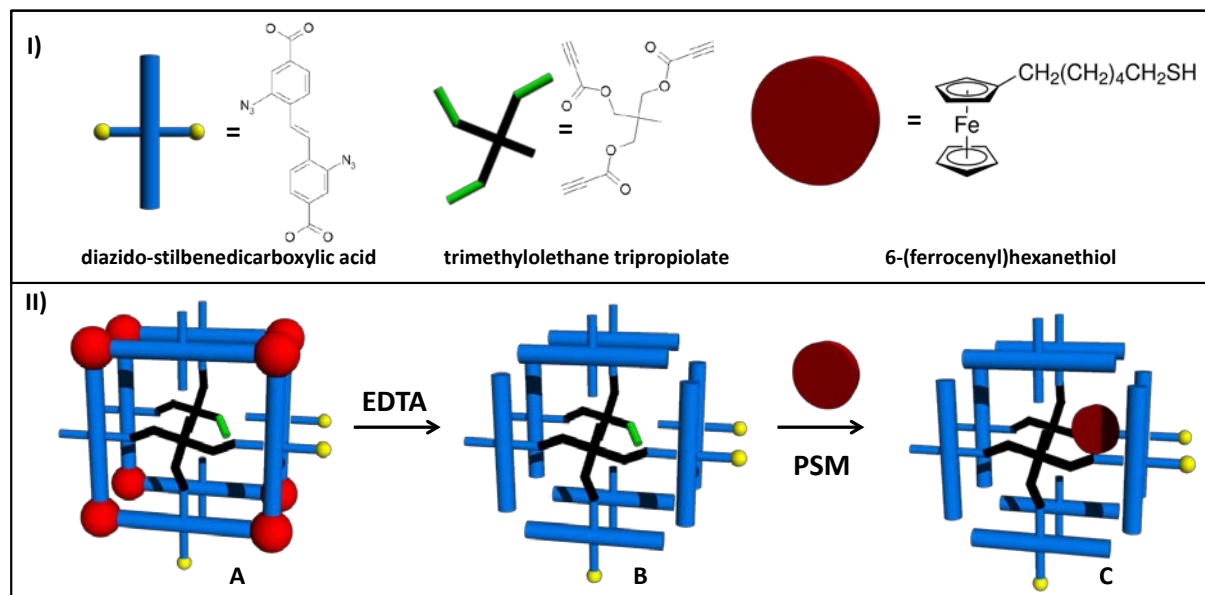


Figure ESI1. Top: Chemical structures of the organic tectons of the SURGEL and of the ferrocenyl derivative used for the PSM. Bottom: Scheme of the steps involved in the preparation of the SURGEL and of PSM.

Post-Synthetic modification (PSM) of SURGEL: The pristine SURGEL was immersed in an ethanolic solution of 6-(ferrocenyl)hexanethiol at 50C for 5 days and then irradiated at 254 nm for 20 minutes under argon. The sample was then thoroughly rinsed with ethanol to remove any unreacted ferrocenyl derivative and dried under gentle nitrogen flow.

Cyclic Voltammetry (CV): The CV measurements have been performed under inert gas. Potentiostat: PalmSens³, from Palm Sens. The cyclic voltammetry was carried out using the electrochemical cell in Scheme ESI1. As supporting electrolyte the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoronethylsulfonyl)-imide ([BMIM][NTf₂]) from IoLiTec has been used. As electrolyte dissolved in the IL ferrocene 2.85mM has been used, unless otherwise stated in text. At least 4 scans have been recorded for each measurement and they show no substantial change in shape. The second cycle is always represented.

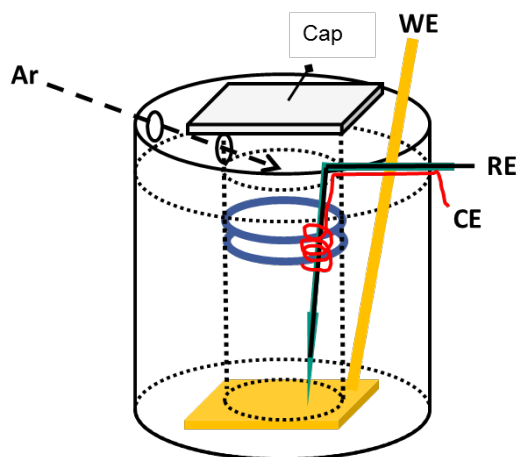


Figure ESI2. Three electrodes set up: RE and CE: reference electrode, Pt wire. WE: working electrode.

X-Ray photoemission spectroscopy (XPS): All spectra were recorded using a hemispherical electron analyzer (VG Scienta R4000) and a non-monochromated Al K_α X-ray source operated at 300 W. The measurements were performed under ultrahigh vacuum conditions ($1 \cdot 10^{-9}$ mbar) with the pass energy of the electron analyzer set to 200 eV. Spectra were recorded in normal emission (red traces) unless otherwise stated.

ESI 2. IRRA spectra.

The IRRA spectra were recorded on a Bruker VERTEX 80 FTIR spectrometer. Perdeuterated hexadecanethiol-SAMs on Au/Si were used for reference measurements.

IRRA spectra were taken before and after the PSM reaction, carried out as described in ESI1. As clearly observable in Fig. ESI3, after the PSM typical absorption bands of the 6-(ferrocenyl)hexanethiol² are observed (vibration of the CH₂ of the alkyl chain -2856 and 2930 cm⁻¹- as well as, very weak, of the CH of the aromatic ring of the ferrocene, 1105 and 998 cm⁻¹) appear, giving a direct evidence of the success of the PSM reaction. In addition, the absorption band at 3256 cm⁻¹ from the CH stretching of the residual alkyne group appears strongly decreased after PSM (reduced of *ca* 80%), together with the absorption band at 2119 cm⁻¹ to which both the azide and the alkyne functional groups contribute (reduced of *ca* 60%).

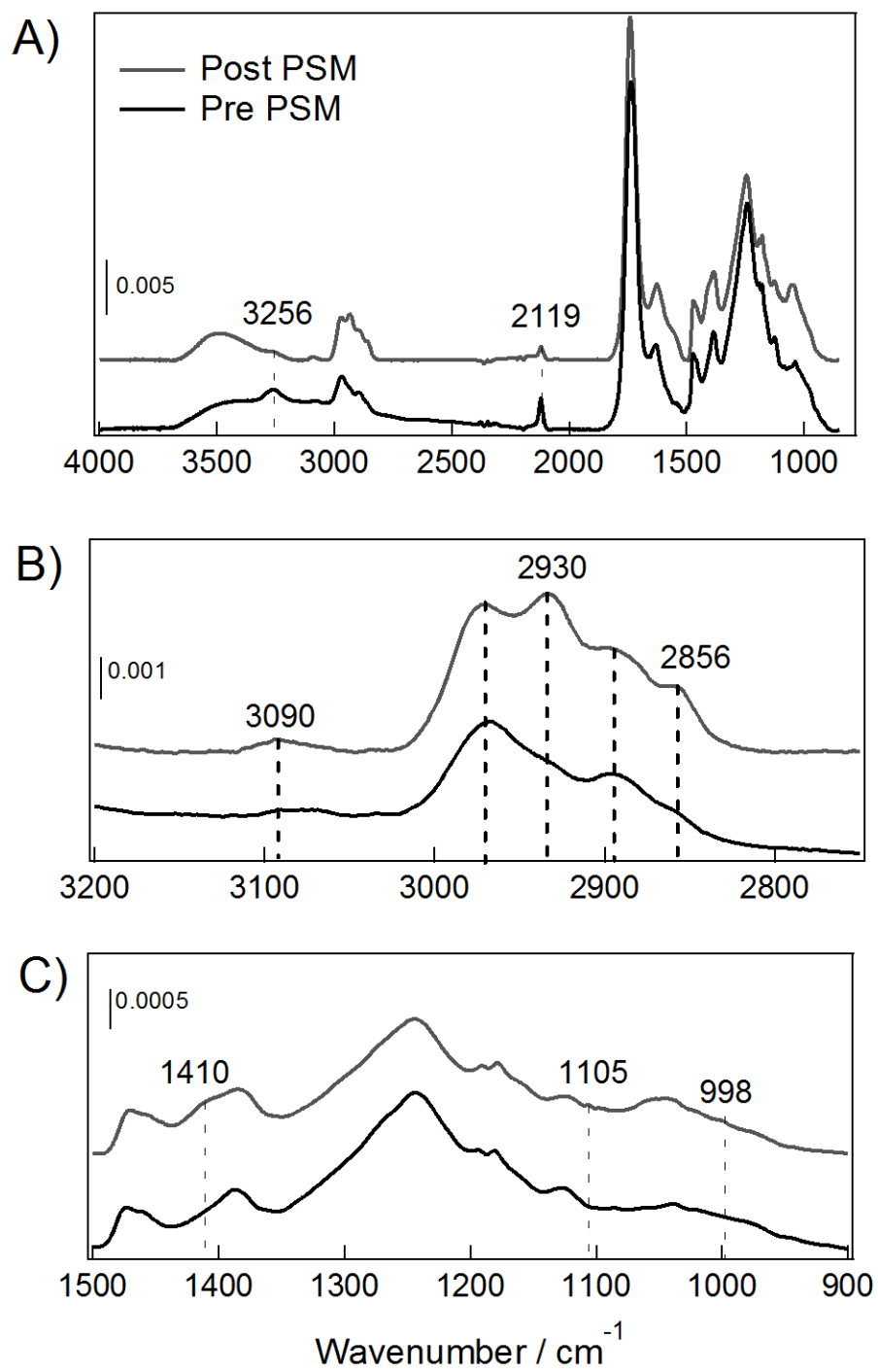


Figure ES13. IRRA spectra of the as prepared SURGEL (black) and of the ferrocenyl modified SURGEL (grey) after background subtraction.

ESI 3. XPS of SURGEL after PSM.

From the survey spectrum (Fig. ESI4, red) all the absorption corresponding to the elements present in the samples are observed. Changing the emission angle to 70° (Fig. ESI4, black) results in loss of intensity in the Au4f signal without major changes in the other signals. This evidence supports that the ferrocenyl derivative is not decorating only the top layer, but rather it is indeed inside the SURGEL.

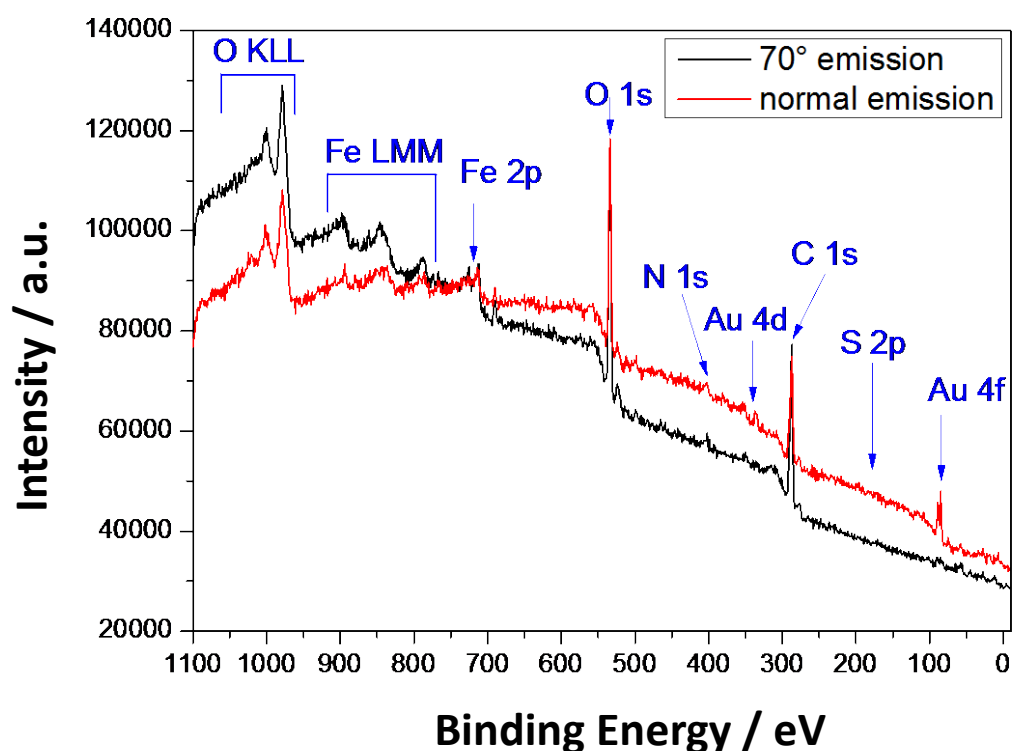


Figure ESI4. Survey XP spectra recorded at normal emission (in red) and 70° (in black).

Figure ESI5 shows the XP spectra of the Fe 2p, S 2p, N 1s and C 1s regions. The intensity (i.e. the peak area after background subtraction) has been used to determine the stoichiometric ratio between Fe, C, S and N. The ratios C/Fe (26) and N/S (2,5) gives values very close to the expected ones for two ferrocene per alkyne moiety (30 and 3, respectively).

Fe 2p: Two signals stemming from the Fe 2p_{3/2} (binding energy of 711 eV) and the Fe 2p_{1/2} (binding energy of 725 eV) orbitals are discernible. Due to the uneven background, only the contribution of the Fe 2p_{3/2} line was used for determination of the peak area (i.e., the intensity) for the stoichiometry calculations.

N 1s: Due to the limited energy resolution, only one feature with a binding energy of 401.5 eV can be resolved, although one would expect two features with an intensity ratio of 2:1.

S 2p: Due to the limited energy resolution, only one feature with a binding energy of 169.6 eV can be resolved, although one would expect two features (2 p_{3/2} and 2 p_{1/2}).

C 1s: Two rather broad components stemming from chemically inequivalent carbon moieties are clearly discernible (tentatively assigned to carbon atoms bound to electronegative species like N and O with a binding energy of ca. 290 eV and the remaining C bound only to C and H exhibiting a binding energy of around 286 eV).

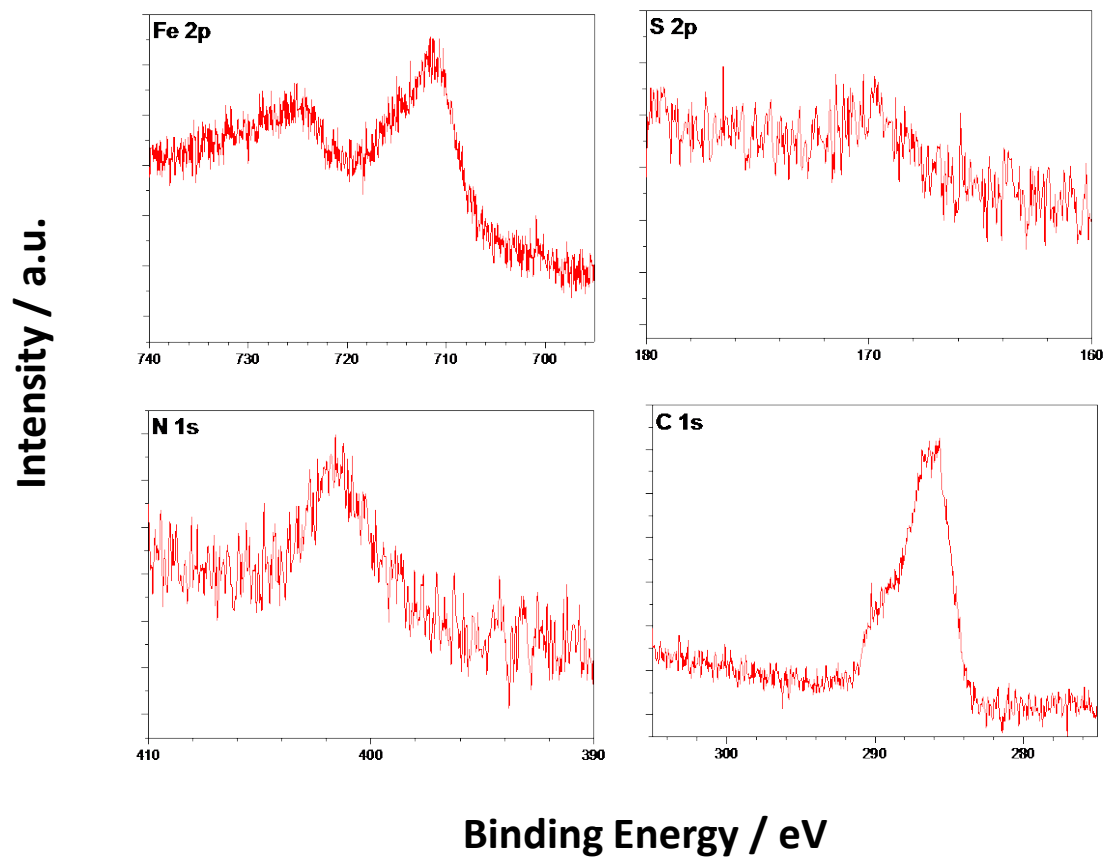


Figure ES15. XP spectra recorded at normal emission for Fe 2p, S 2p, N 1s and C 1s.

ESI 4. Cyclic voltamograms of ferrocene post-synthetic modified SURGEL at different scan rates in neat ionic liquid.

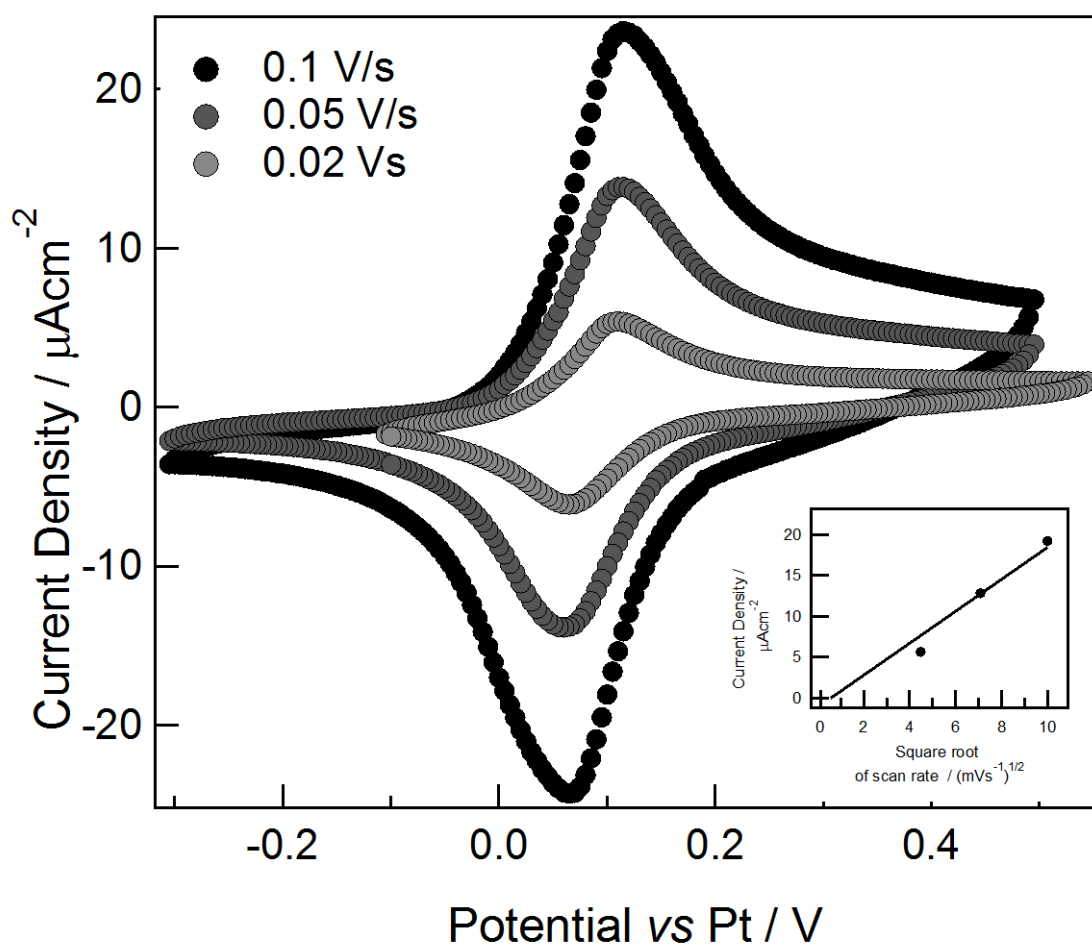


Figure ES16. CV of SURGEL after PSM in neat ionic liquid at different scan rates. In the inset, the linear dependence of the current density vs the square root of the scan rate.

ESI 5. Cyclic voltamograms of ferrocene post-synthetic modified SURGEL at different scan rates in the presence of ferrocene in ionic liquid.

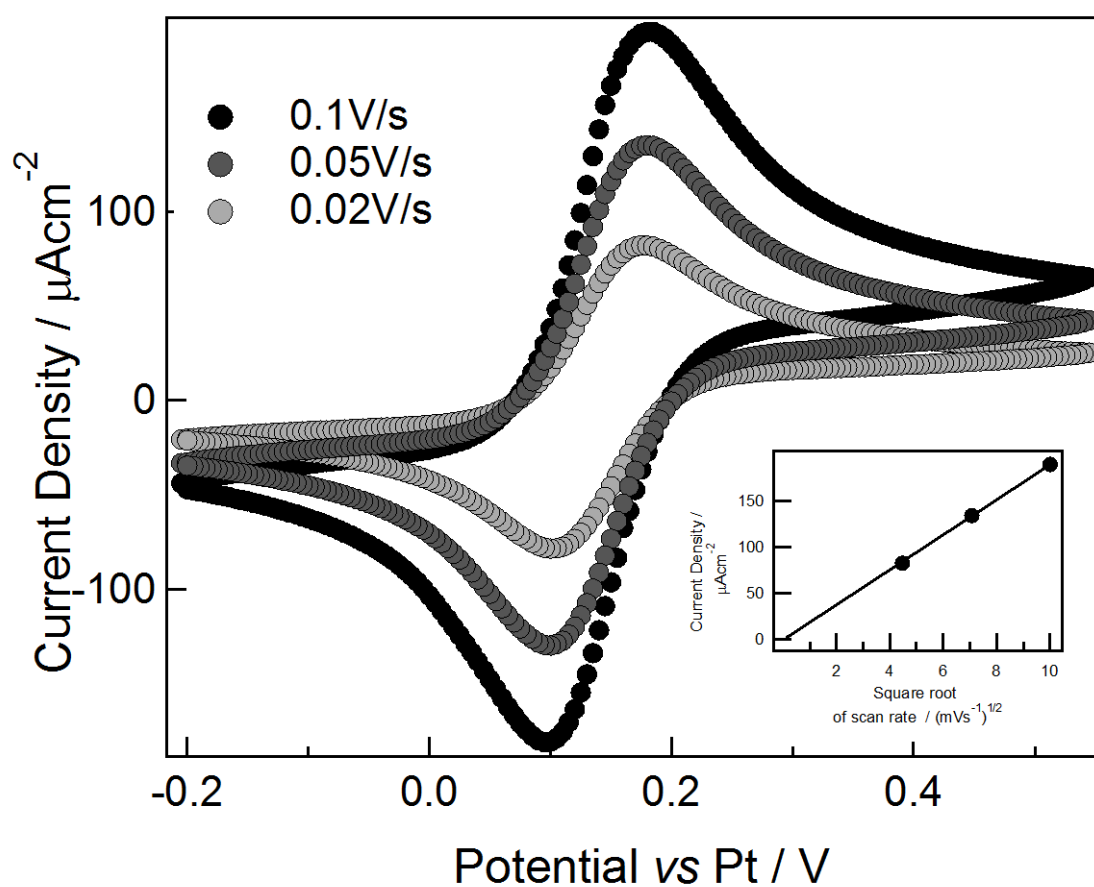


Figure ES17. CV of SURGEL after PSM in ionic liquid and 2.85mM ferrocene at different scan rates. In the inset, the linear dependence of the current density vs the square root of the scan rate.

- 1 M. Tsotsalas, J. Liu, B. Tettmann, S. Grosjean, A. Shahnas, Z. Wang, C. Azucena, M. Addicoat, T. Heine, J. Lahann, J. Overhage, S. Bräse, H. Gliemann, C. Wöll, *J. Am. Chem. Soc.*, 2014, **136**, 8.
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