

Supporting Information:

Formic acid electro-synthesis from carbon dioxide in a room temperature ionic liquid†

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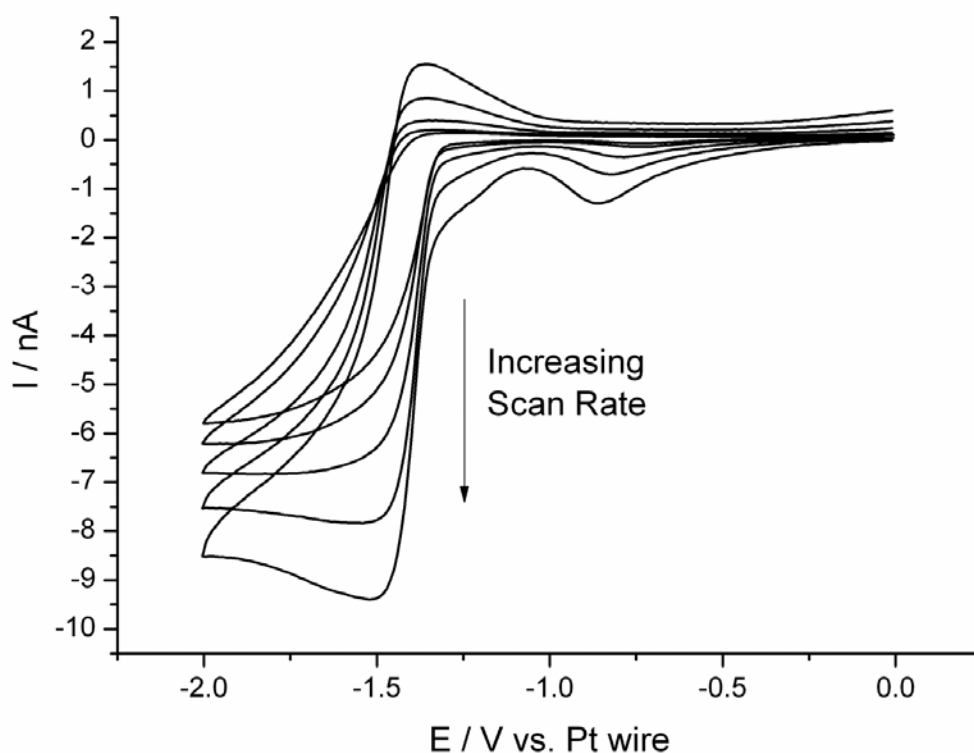


Fig. 5 Scan rate study of 100mM H[NTf₂] in [C₂mim][NTf₂] on a pre-anodised Pt microelectrode (50, 100, 200, 400, 800mVs⁻¹).

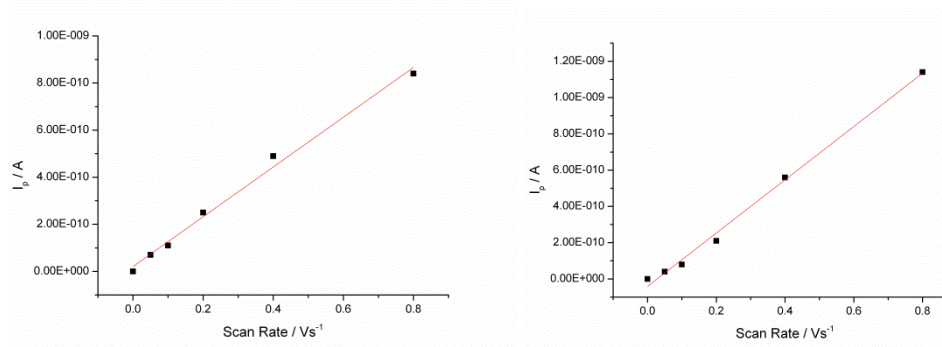
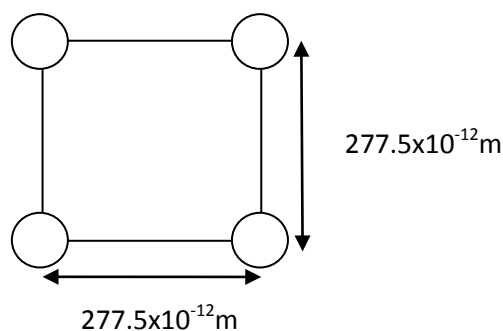


Fig. 6 Plots of peak current against scan rate for surface platinum oxide reduction (left) and surface hydrogen oxidation (right).

The charge (area divided by scan rate) underneath the peak corresponding to oxidation of surface hydrogen atoms was determined to be $2.5 \times 10^{-10} \text{C}$. The microdisc electrode was calibrated to be of radius $6.4 \mu\text{m}$, resulting in the charge density underneath this feature being 1.9Cm^{-2} . Using the Pt-Pt bond length in polycrystalline platinum of $277.5 \times 10^{-12} \text{m}$ and the approximation of the surface structure shown below, the surface density of Pt atoms is $1.3 \times 10^{19} \text{atoms m}^{-2}$. For the electrode in question and assuming a surface layer of one H atom per Pt, this corresponds to a monolayer oxidation charge of $2.5 \times 10^{-10} \text{C}$. Hence this feature is consistent with a monolayer coverage of H on Pt.



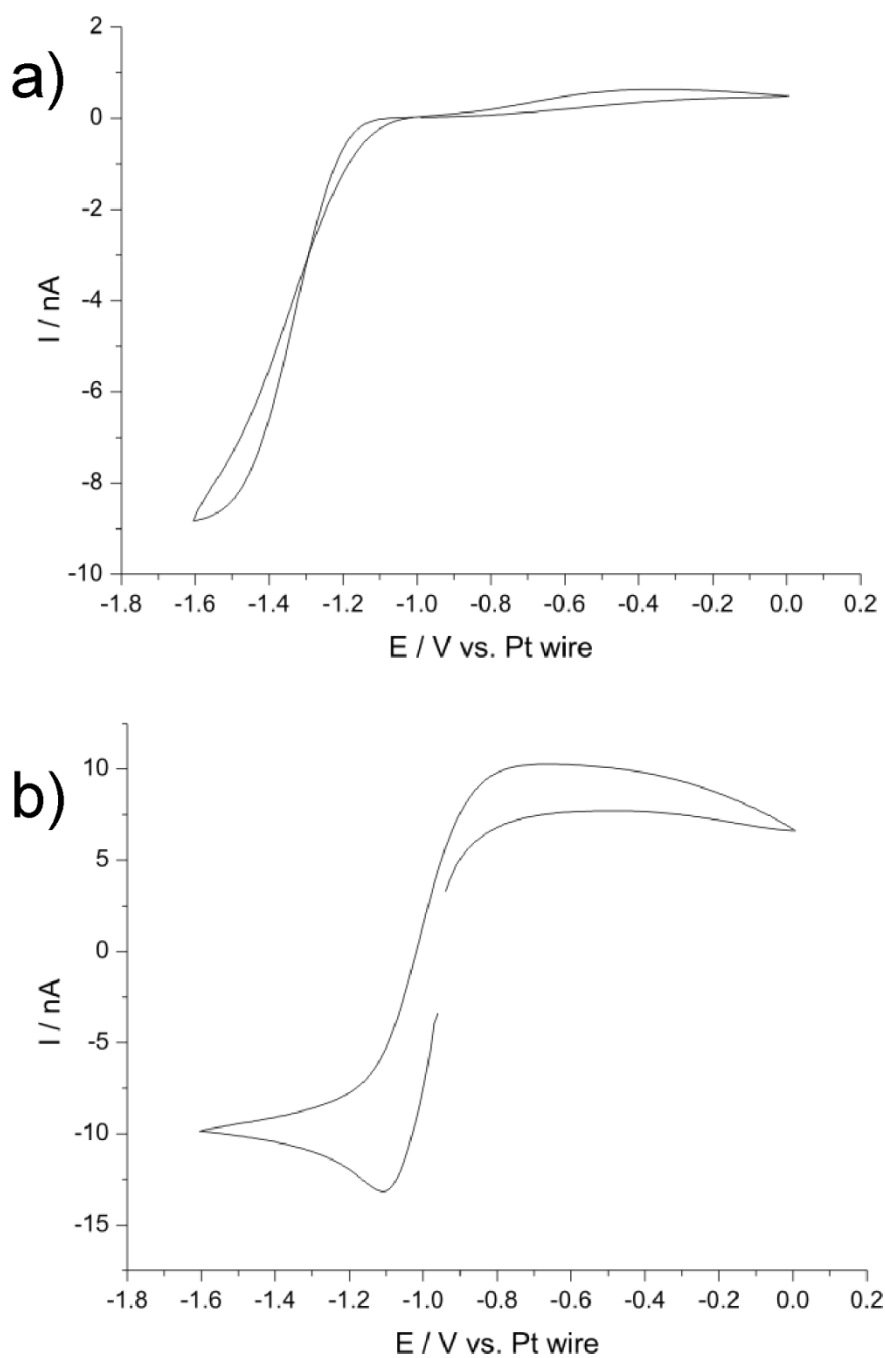


Fig. 7 100 mVs⁻¹ CV of 100mM H[NTf₂] in [C₂mim][NTf₂] on a Pt microelectrode under H₂ atmosphere (a) without and (b) with pre-anodisation of the electrode surface.

The cyclic voltammetry of the mixture of H[NTf₂] and H₂ in [C₂mim][NTf₂] illustrates clearly the change from irreversible to reversible behaviour and is further evidence for the proposed change in mechanism as described previously. In Figure 7a there is a large separation between the reduction of H⁺ and oxidation of H₂, whereas in Figure 7b there is a continuous wave.

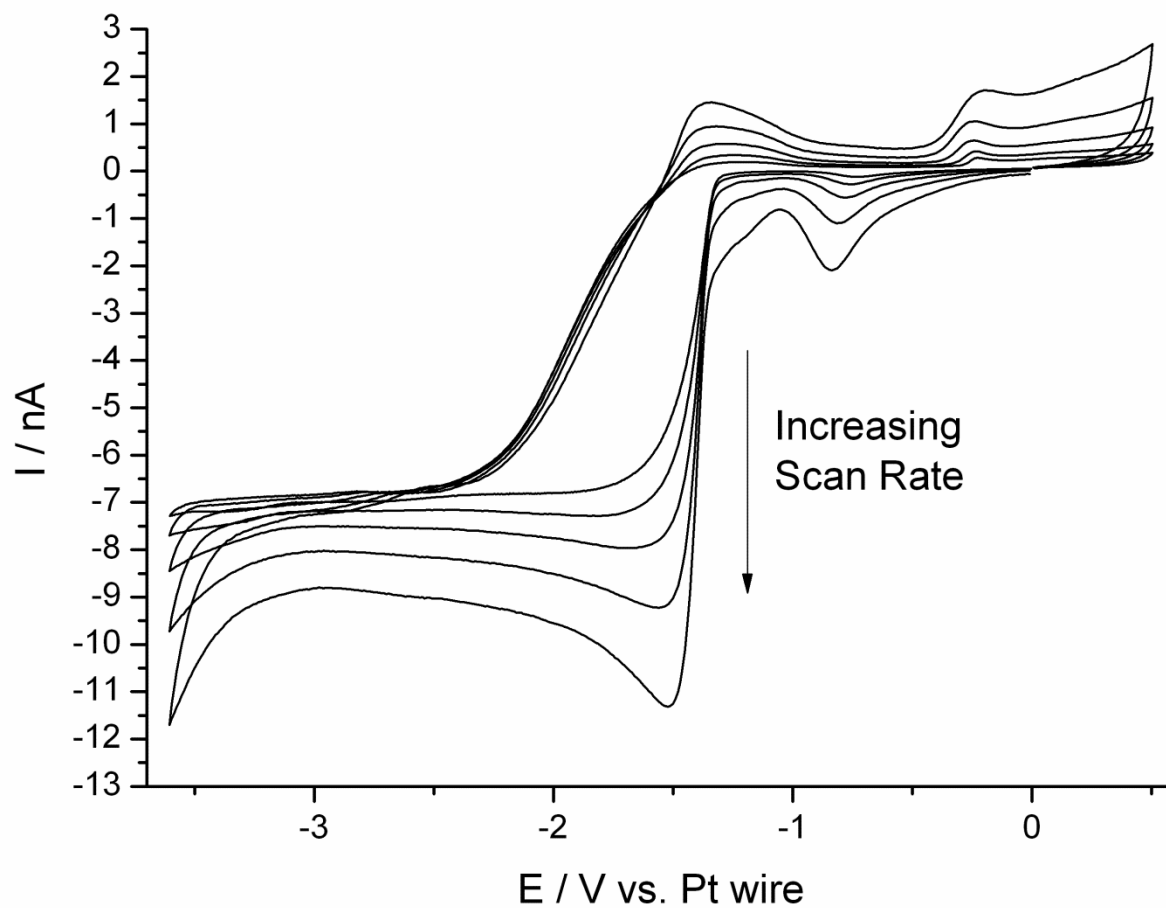


Fig. 8 Scan rate study of 100mM H[NTf₂] in [C₂mim][NTf₂] on a pre-anodised Pt microelectrode under a CO₂ atmosphere (50, 100, 200, 400, 800mVs⁻¹).

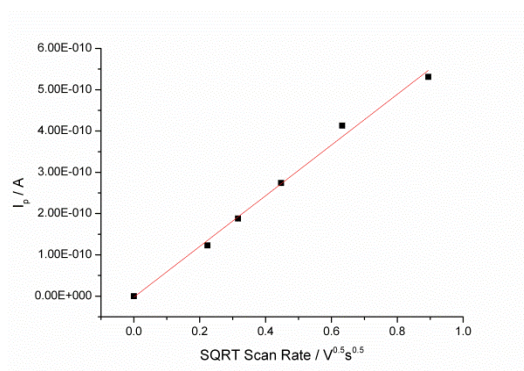


Fig. 9 Plots of peak current against square root scan rate for formic acid oxidation.

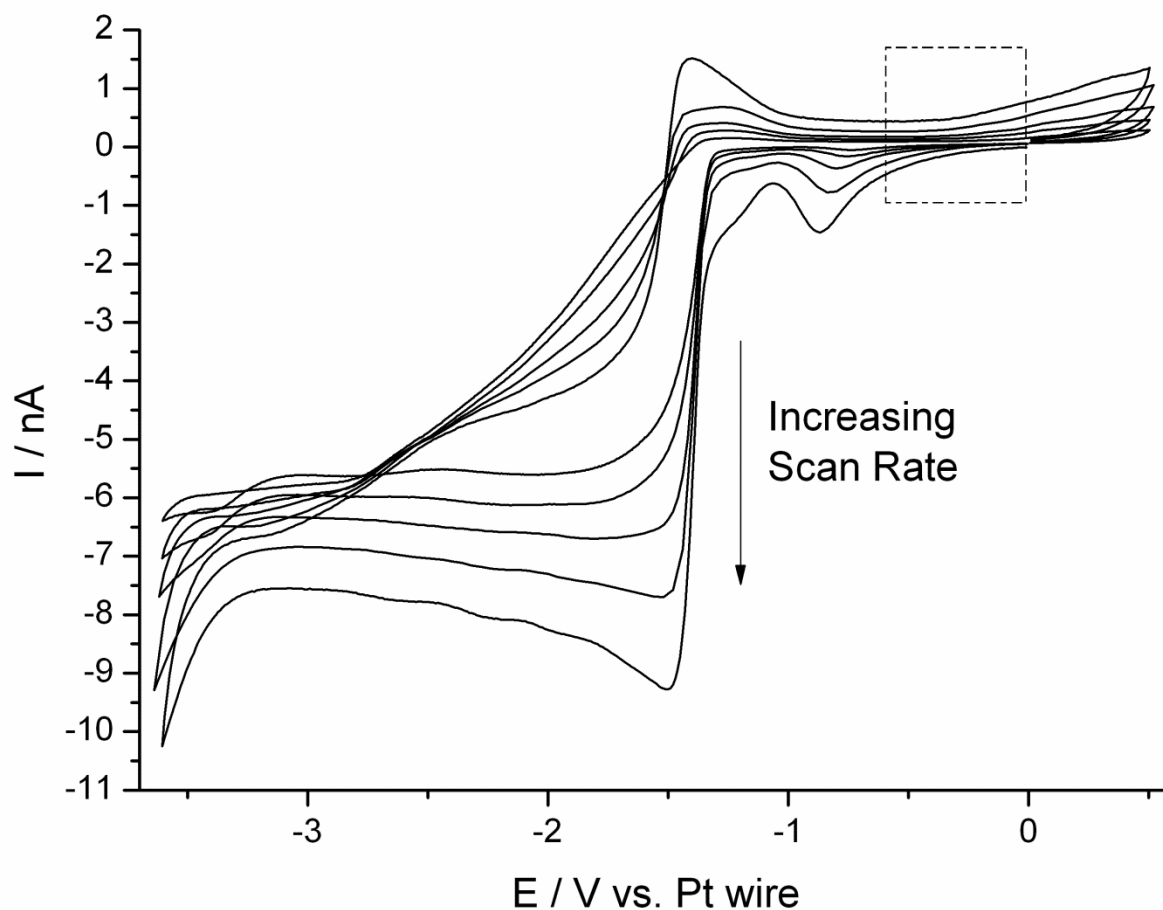


Fig. 10 Scan rate study of 100mM H[NTf₂] in [C₂mim][NTf₂] on a pre-anodised Pt microelectrode under vacuum conditions (50, 100, 200, 400, 800mVs⁻¹).

The highlighted area in Figure 9 indicates the absence of the formic acid oxidation when the experiment is under vacuum conditions, in contrast to Figure 8. The rise in current between 0 and +0.5V is due to the beginning of surface oxidation which takes off rapidly above this potential. The reductive feature beginning at c. -3.4V is the beginning of solvent breakdown.

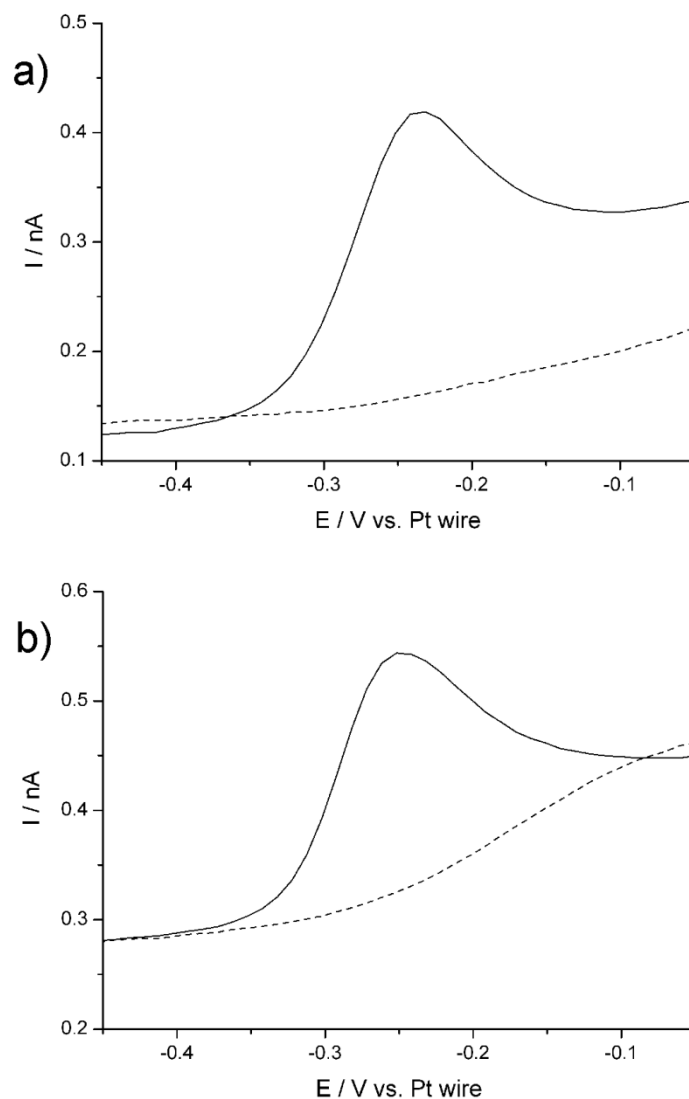


Fig. 11 Formic acid oxidation region of 100 mVs^{-1} CV of $100\text{mM H[NTf}_2\text{]}$ in $[\text{C}_2\text{mim}][\text{NTf}_2]$ on a pre-anodised Pt microelectrode under a) CO_2 atmosphere (solid) followed by vacuum (dashed) and b) CO_2 atmosphere (solid) followed by Ar atmosphere (dashed).

Figure 11 shows the formic acid oxidation region of $100\text{mM H[NTf}_2\text{]}$ in $[\text{C}_2\text{mim}][\text{NTf}_2]$ under various conditions after potentials have been swept through to the same negative potential which effects CO_2 reduction. It demonstrates the absence of formic acid oxidation when the experiment is under vacuum conditions and argon atmosphere rather than CO_2 atmosphere. This eliminates the possibility of this feature being the oxidation of a product of solvent breakdown or of an impurity entering the gas stream, confirming that it is a product of CO_2 reduction.

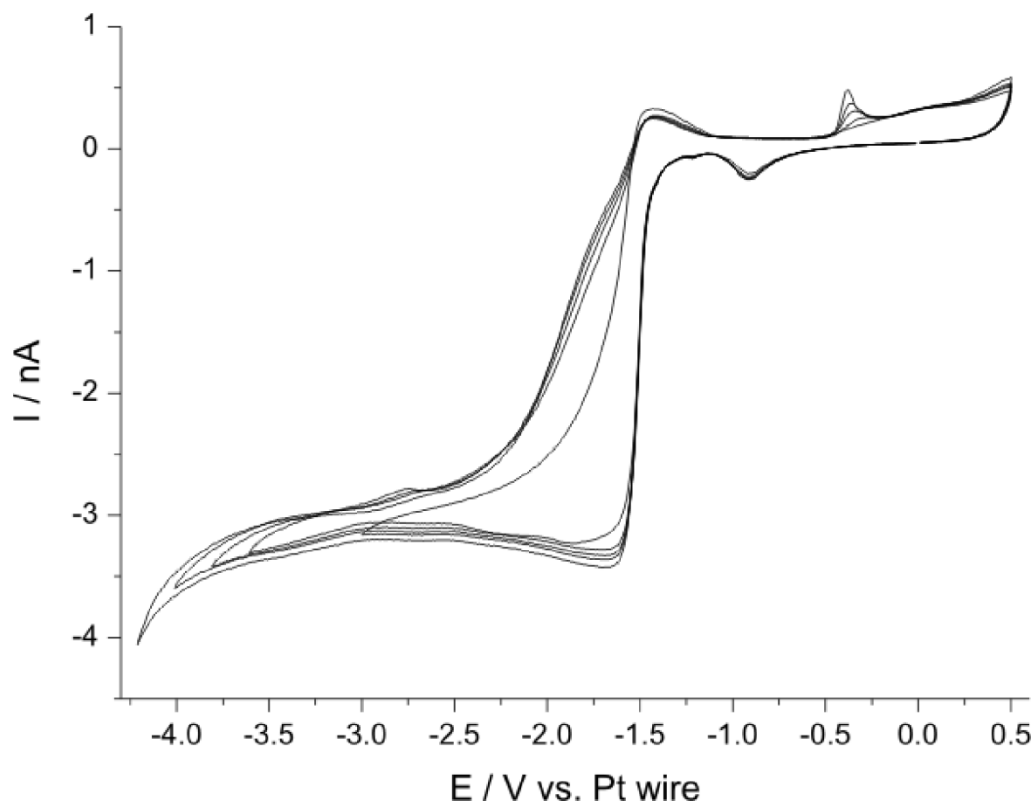


Fig. 12 100 mVs⁻¹ CVs of 100mM H[NTf₂] in [C₄mpyrr][NTf₂] on a pre-anodised Pt microelectrode under a CO₂ atmosphere.

Analogous observations occur when the previous experiments are repeated in the RTIL [C₄mpyrr][NTf₂]. The CVs are similar to Figure 2 and show the growth of a formic acid oxidation peak as the overpotential of CO₂ reduction is increased. The wider electrochemical window of [C₄mpyrr][NTf₂] compared to [C₂mim][NTf₂] allows for greater reduction of CO₂ in the voltammetry and so a larger oxidation current of formic acid is observed when scanning more negative.

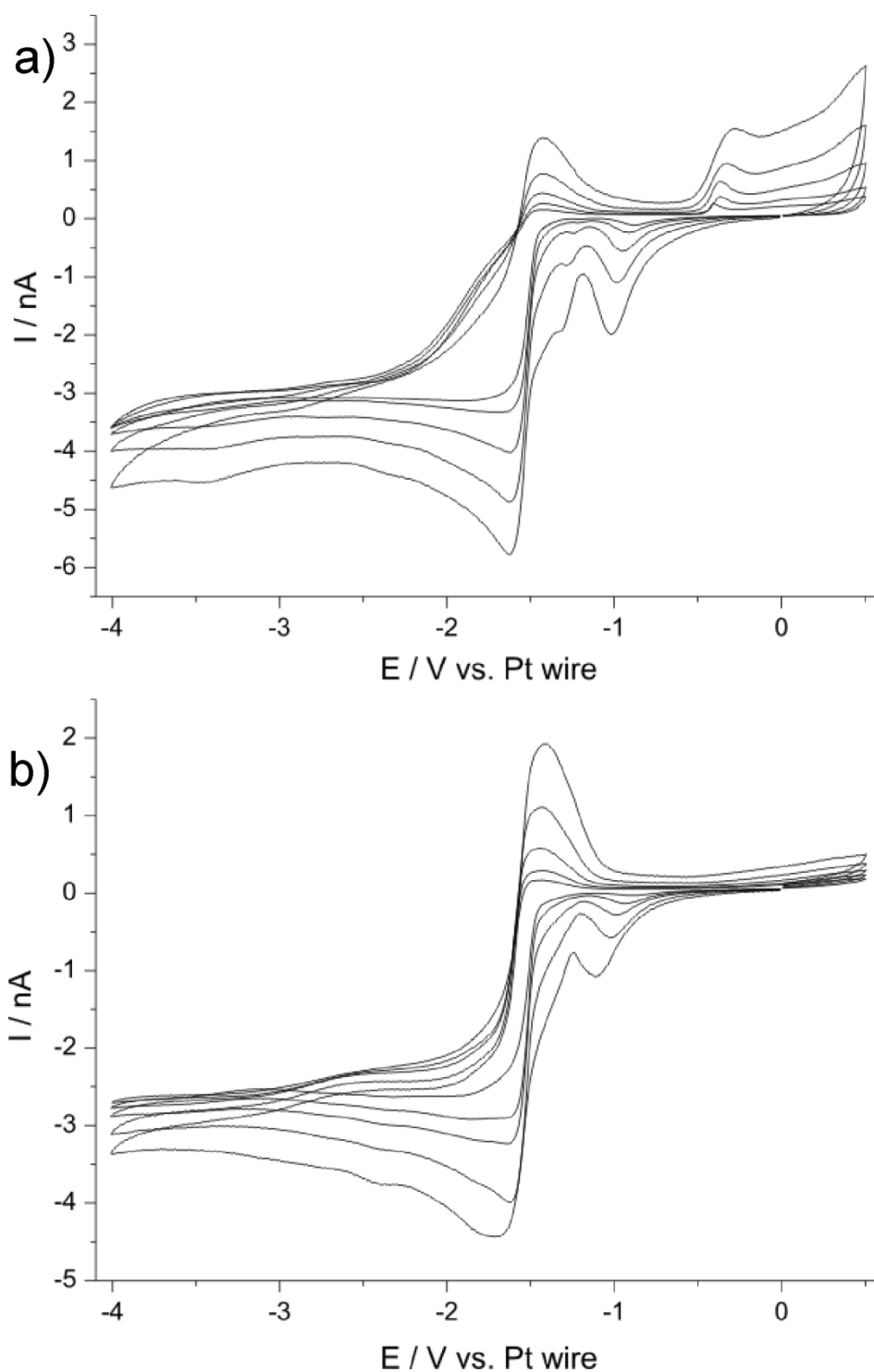


Fig. 13 Scan rate study (50, 100, 200, 400, 800mVs⁻¹) of 100mM H[NTf₂] in [C₄mpyrr][NTf₂] on a pre-anodised Pt microelectrode under a) CO₂ atmosphere and b) vacuum conditions.

Figure 13 again demonstrates that under vacuum conditions the product formic acid is not formed. It can be clearly seen from this data that the wider electrochemical window of [C₄mpyrr][NTf₂] gives a greater separation of the CO₂ reduction and solvent breakdown features. CO₂ reduction can be seen at c. -3.4V in Figure 13a, whilst under vacuum in Figure 13b no feature is seen in this potential range.

Experimental Procedures

All electrochemical experiments were performed using an Autolab potentiostat (Eco-Chemie). A two electrode setup was employed involving a Pt working electrode (6.4 μm radius, calibrated by CV and chronoamperometry using the Fc/Fc⁺ redox couple in MeCN with $D = 2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) and a Pt wire counter/quasi-reference. The working electrode was polished on soft lapping pads (Buehler) topped with alumina slurries in the order 1.0 μm , 0.3 μm and 0.05 μm and then sonicated in distilled water to remove any stuck particles. The Pt wire was cleaned in a blue bunsen flame. Both were rinsed with acetonitrile and dried prior to use. A disposable micropipette tip was attached to the working electrode and used as the cell container into which 30 μl of RTIL was injected. The cell was then placed inside a glass T-shaped cell in which conditions can be changed easily between vacuum and gas atmospheres.¹ Samples were purged under vacuum to remove trace atmospheric gases and water present in the RTIL.¹ CO₂, Ar and H₂ (BOC) were dried through a CaCl₂/molecular sieve (3-4Å) mixture and left to saturate the solution for 1hr. The Faraday cage was thermostatted to 298K. The [C₂mim][NTf₂] was provided by QUILL, Belfast and prepared following standard literature procedures. The H[NTf₂] (>95%) was obtained from Sigma-Aldrich and the HCO₂H (98-100%) from BDH Chemicals.

Reference

1. D. S. Silvester and R. G. Compton, *Z. Phys. Chem.*, 2006, **220**, 1247-1274.