Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for

The Hydrogen Evolution Reaction in a Room Temperature Ionic Liquid: Mechanism and Electrocatalyst trends

Yao Meng,[a] *Leigh Aldous,*[a,b] *Stephen R. Belding*[a] *and Richard G. Compton*[a,*]

[a] Department of Chemistry, Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom

[b] School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia

1. The details of voltammetry over a range of $H[NTf_2]$ concentration, metals and scan rate studies (Experiment data (-) and optimization of theoretical curve (o)) vs Ag/Ag^+ reference redox couple

1.1.1. $H[NTf_2]$ reduction only on Pt electrode in $[C_2mim][NTf_2]$

ν= 100, 400, 800mV s^{-1}

E_f=-0.35 V

D_c=2.5e-7 cm^2s^{-1}

D_a=5.5e-6 cm^2s^{-1}

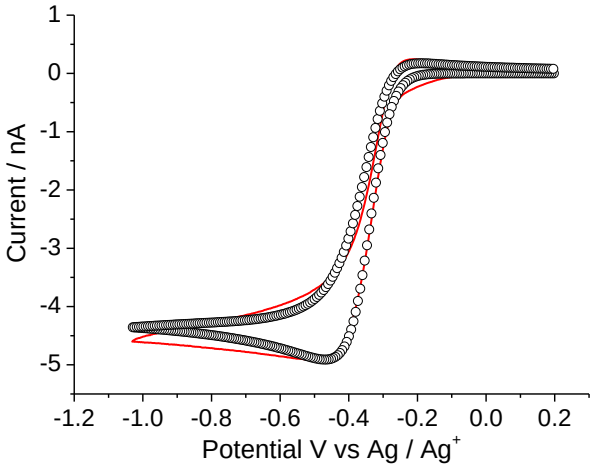
C_c=75mM

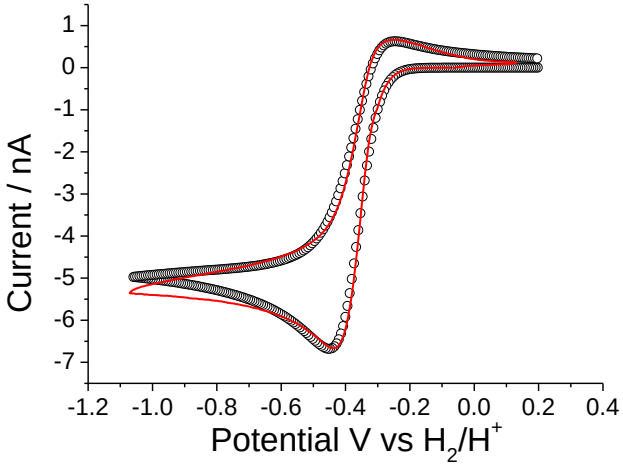
k^0_c=2.7e-3 cm s^{-1}

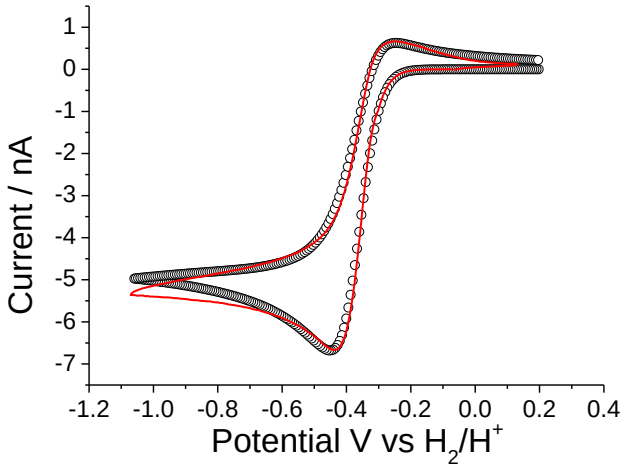
r=5.25e-4 cm

α=0.5

β=0.5







1.1.2. Hydrogen oxidation only on Pt electrode in $[C_2mim][NTf_2]$

ν= 100, 400, 800mV s^{-1}

E_f=-0.31V

D_c=5.5e-6 cm^2s^{-1}

D_a=2.5e-7 cm^2s^{-1}

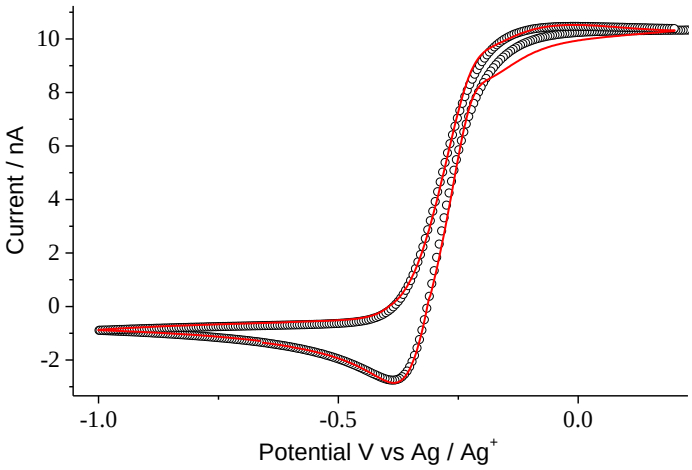
C_c=9.1mM

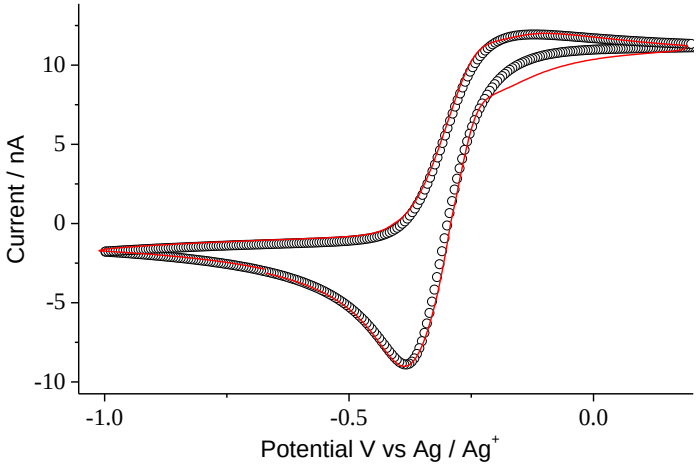
k^0_a=1.1e-2 cm s^{-1}

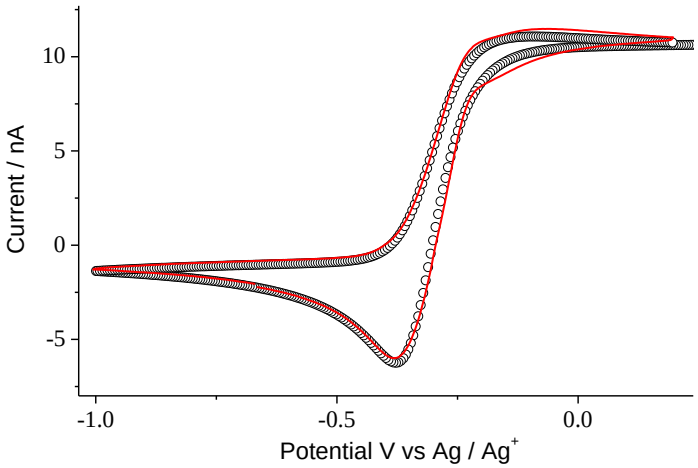
r=5.25e-4 cm

α=0.5

β=0.5



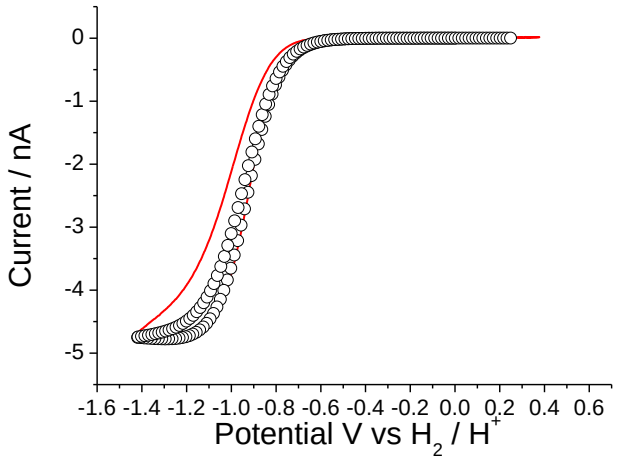




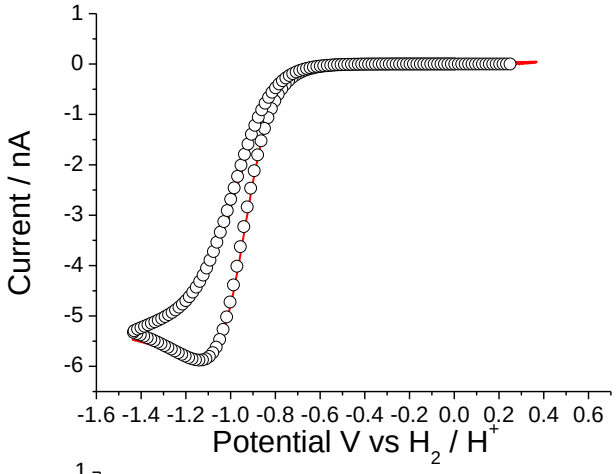
1.2 H[NTf_2] concentration study on gold in [C_2mim][NTf_2])

1.2.1. 89mM H[NTf_2] on gold in [C_2mim][NTf_2])

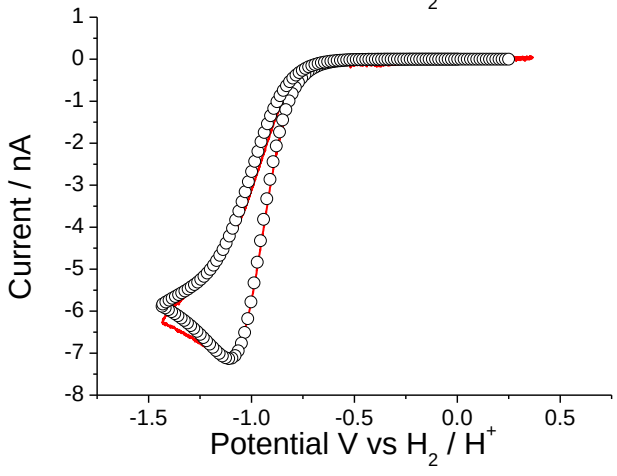
Au
Scan rate: 100mV/s
Potential window (V): (-1.45, 0.25)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Au}$: 4.6e-4 cm
α: 0.35
k^o : 3e-7 cm s^{-1}
C: 89 mM
E_f : -0.3506 V



Au
Scan rate: 400mV/s
Potential window (V): (-1.45, 0.25)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Au}$: 4.6e-4 cm
α: 0.35
k^o: 3e-7 cm s^{-1}
C: 89 mM
E_f : -0.3506 V

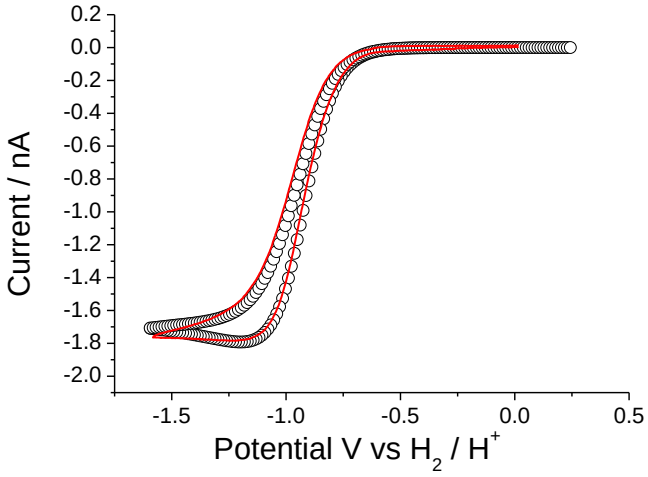


Au
Scan rate: 1V/s
Potential window (V): (-1.45, 0.25)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Au}$: 4.6e-4 cm
α: 0.35
k^o: 3e-7 cm s^{-1}
C: 89 mM
E_f : -0.3506 V

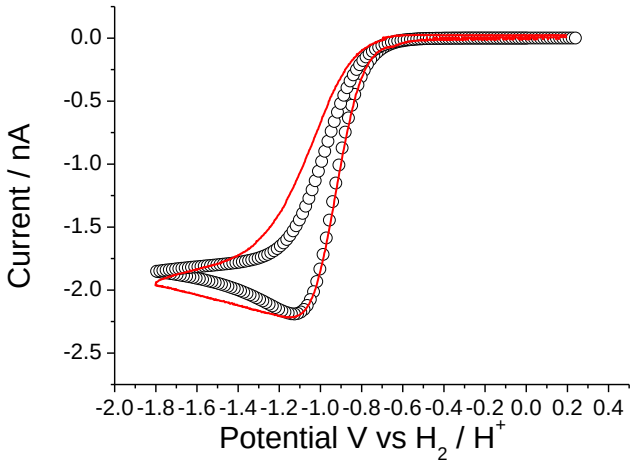


1.2.2. 33mM H[NTf_2] on gold in [C_2mim][NTf_2])

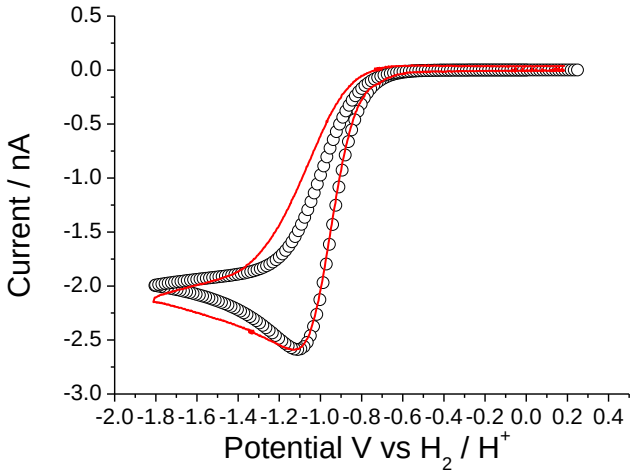
Au
Scan rate: 100mV/s
Potential window (V): (-1.55, 0.25)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Au}$: 4.6e-4 cm
α: 0.35
k^o : 3e-7 cm s^{-1}
C: 33 mM
E_f : -0.3506 V



Au
Scan rate: 400mV/s
Potential window (V): (-1.55, 0.25)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Au}$: 4.6e-4 cm
α: 0.35
k^o : 3e-7 cm s^{-1}
C: 33 mM
E_f : -0.3506 V

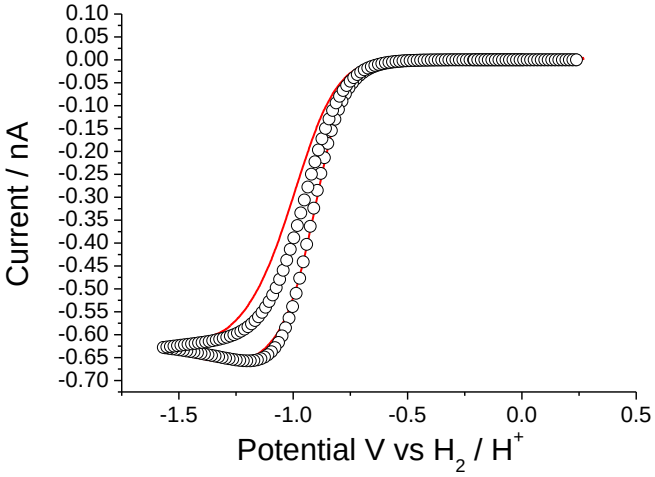


Au
Scan rate: 800mV/s
Potential window (V): (-1.55, 0.25)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Au}$: 4.6e-4 cm
α: 0.35
k^o: 3e-7 cm s^{-1}
C: 33 mM
E_f : -0.3506 V

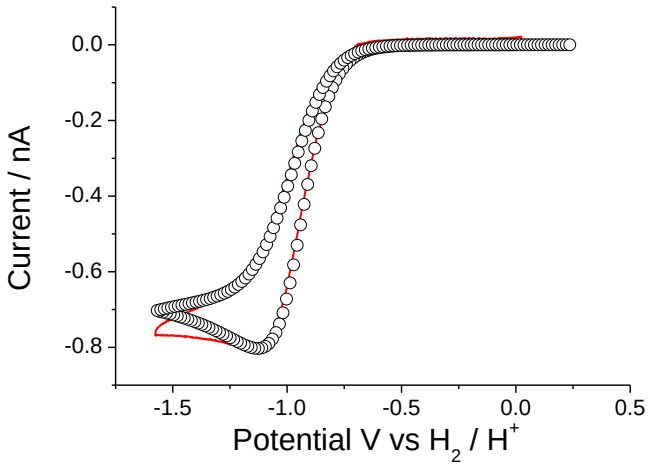


1.2.3. 12mM H[NTf_2] on gold in [C_2mim][NTf_2])

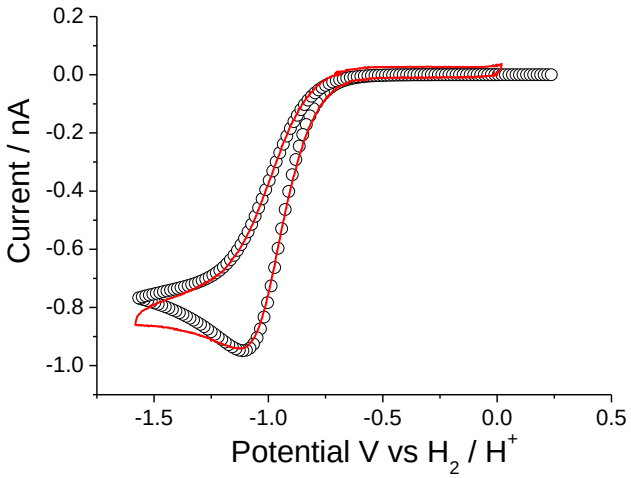
Au
Scan rate: 100mV/s
Potential window (V): (-1.55, 0.25)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Au}$: 4.6e-4 cm
α: 0.35
k^o: 3e-7 cm s^{-1}
C: 12 mM
E_f : -0.3506 V



Au
Scan rate: 400mV/s
Potential window (V): (-1.55, 0.25)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Au}$: 4.6e-4 cm
α: 0.35
k^o : 3e-7 cm s^{-1}
C: 12 mM
E_f : -0.3506 V



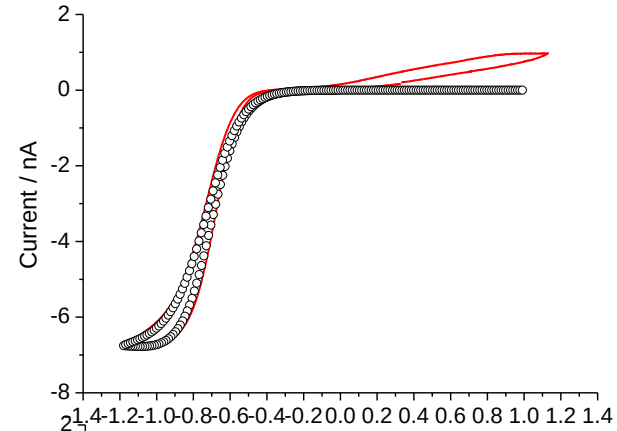
Au
Scan rate: 800mV/s
Potential window (V): (-1.55, 0.25)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Au}$: 4.6e-4 cm
α: 0.35
k^o : 3e-7 cm s^{-1}
C: 12 mM
E_f: -0.3506 V



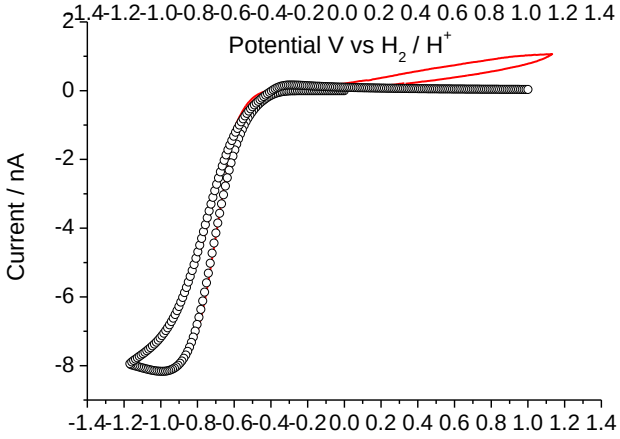
1.3 H[NTf_2] concentration study on molybdenum in [C_2mim][NTf_2])

1.3.1. 95mM H[NTf_2] on molybdenum in [C_2mim][NTf_2])

Mo
Scan rate: 25mV/s
Potential window (V): (-1.2, 1)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Mo}$: 6.5e-4 cm
α: 0.35
k^o : 6.5e-6 cm s^{-1}
C: 95 mM
E_f : -0.3506 V

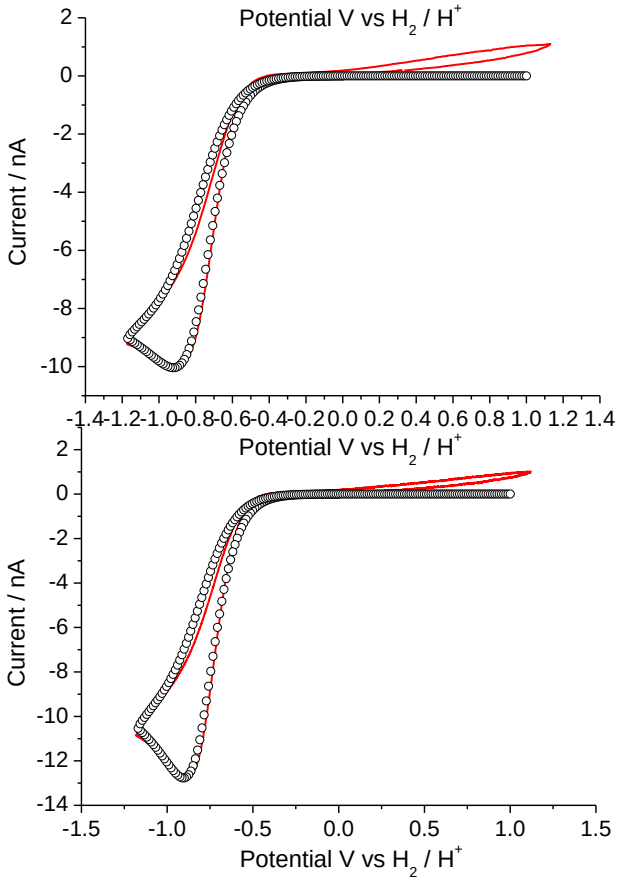


Mo
Scan rate: 100mV/s
Potential window (V): (-1.2, 1)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Mo}$: 6.5e-4 cm
α: 0.35
k^o : 6.5e-6 cm s^{-1}
C: 95 mM
E_f : -0.3506 V



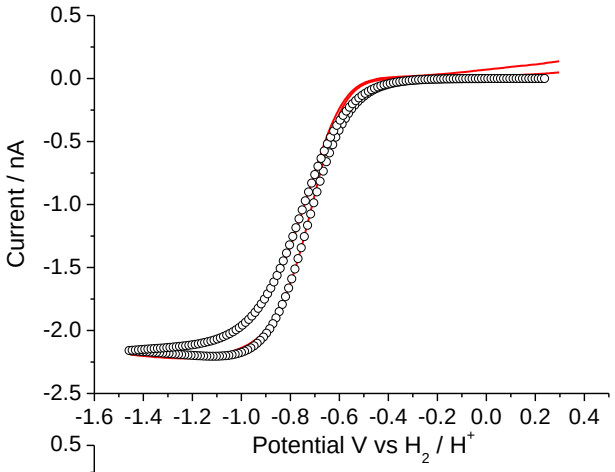
Mo
Scan rate: 400mV/s
Potential window (V): (-1.2, 1)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Mo}$: 6.5e-4 cm
α: 0.35
k^o : 6.5e-6 cm s^{-1}
C: 95 mM
E_f : -0.3506 V

Mo
Scan rate: 800mV/s
Potential window (V): (-1.2, 1)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Mo}$: 6.5e-4 cm
α: 0.35
k^o : 6.5e-6 cm s^{-1}
C: 95 mM
E_f : -0.3506 V

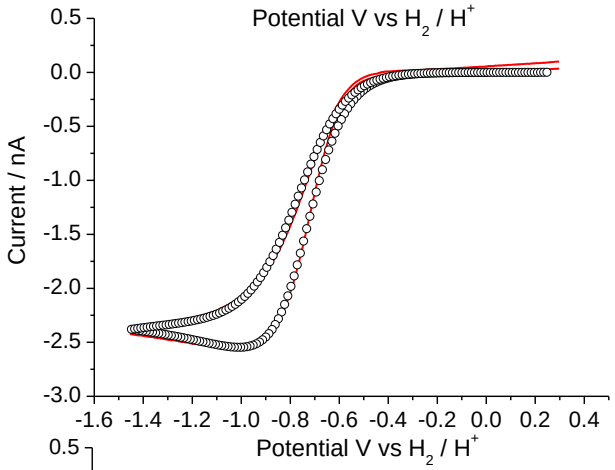


1.3.2. 30mM H[NTf_2] on molybdenum in [C_2mim][NTf_2])

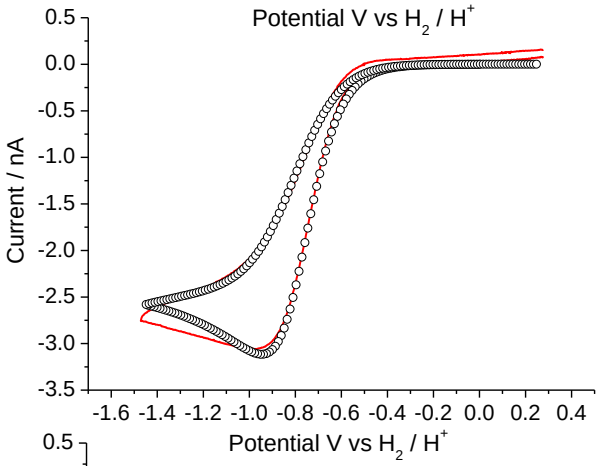
Mo
Scan rate: 25mV/s
Potential window (V): (-1.5, 1)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Mo}$: 6.5e-4 cm
α: 0.35
k^o : 6.5e-6 cm s^{-1}
C: 30 mM
E_f : -0.3506 V



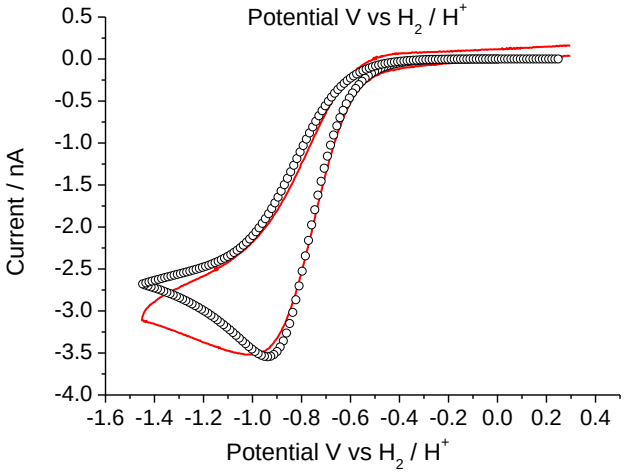
Mo
Scan rate: 100mV/s
Potential window (V): (-1.5, 1)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Mo}$: 6.5e-4 cm
α: 0.35
k^o: 6.5e-6 cm s^{-1}
C: 30 mM
E_f: -0.3506 V



Mo
Scan rate: 400mV/s
Potential window (V): (-1.5, 1)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Mo}$: 6.5e-4 cm
α: 0.35
k^o : 6.5e-6 cm s^{-1}
C: 30 mM
E_f : -0.3506 V

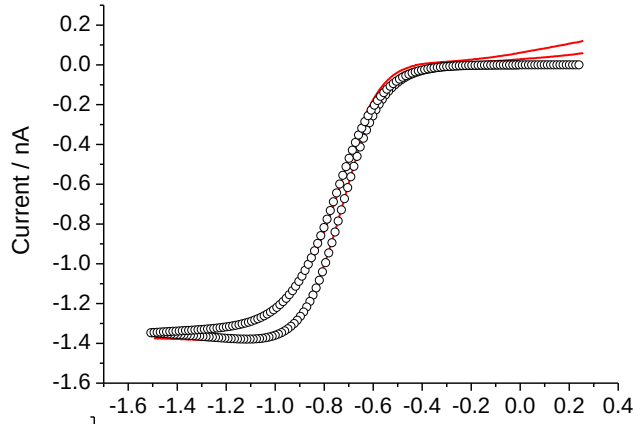


Mo
Scan rate: 800mV/s
Potential window (V): (-1.2, 1)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Mo}$: 6.5e-4 cm
α: 0.35
k^o : 6.5e-6 cm s^{-1}
C: 30 mM
E_f: -0.3506 V

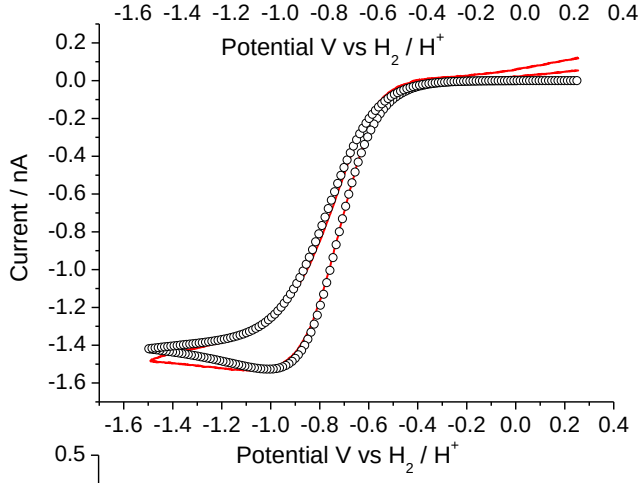


1.3.3. 19mM $H[NTf_2]$ on molybdenum in $[C_2mim][NTf_2]$)

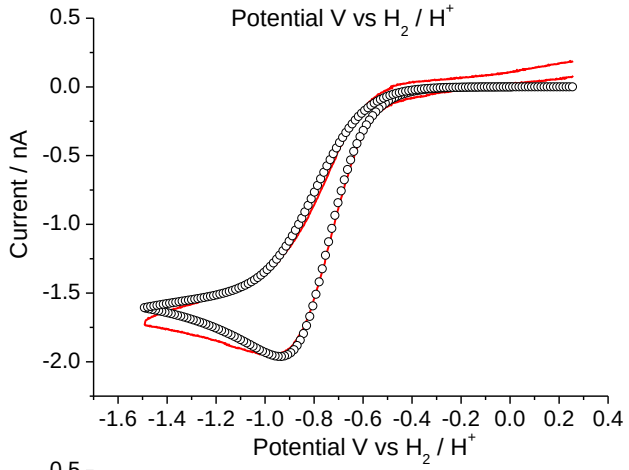
Mo
Scan rate: 25mV/s
Potential window (V): (-1.5, 1)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Mo}$: 6.5e-4 cm
α: 0.35
k^o : 6.5e-6 cm s^{-1}
C: 19 mM
E_f : -0.3506 V



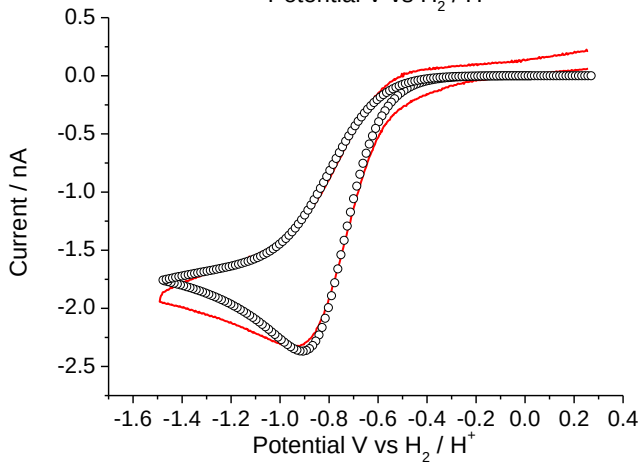
Mo
Scan rate: 100mV/s
Potential window (V): (-1.5, 1)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Mo}$: 6.5e-4 cm
α: 0.35
k^o : 6.5e-6 cm s^{-1}
C: 19 mM
E_f : -0.3506 V



Mo
Scan rate: 400mV/s
Potential window (V): (-1.5, 1)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Mo}$: 6.5e-4 cm
α: 0.35
k^o : 6.5e-6 cm s^{-1}
C: 19 mM
E_f : -0.3506 V

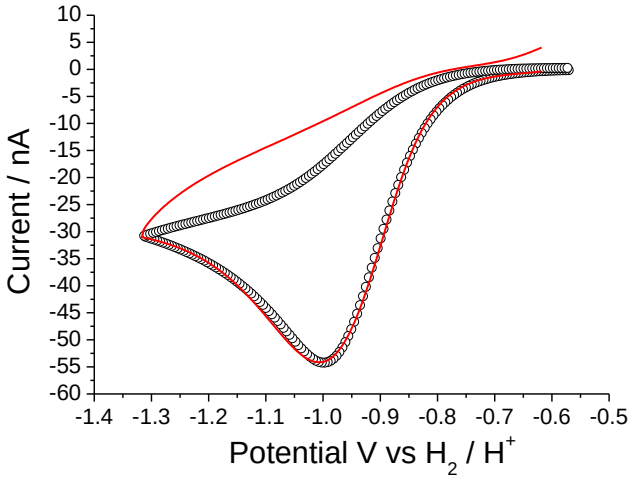


Mo
Scan rate: 800mV/s
Potential window (V): (-1.5, 1)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Mo}$: 6.5e-4 cm
α: 0.35
k^o : 6.5e-6 cm s^{-1}
C: 19 mM
E_f : -0.3506 V

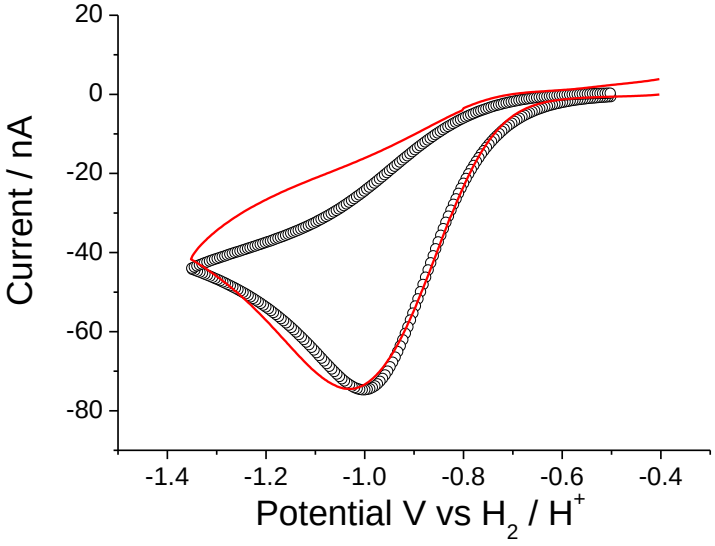


1.4. scan rate study of H[NTf_2] reduction on Nickel in [C_2mim][NTf_2])

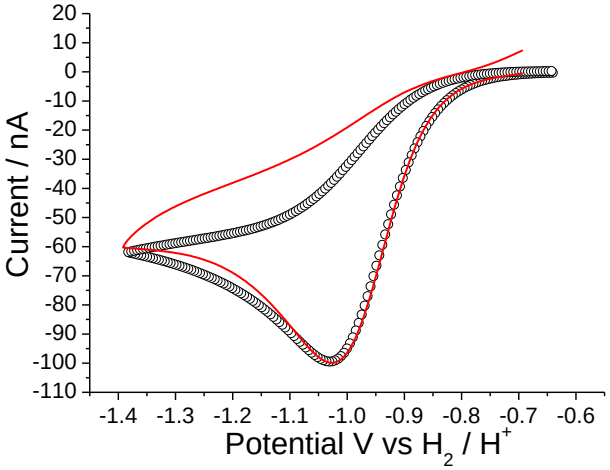
Ni
Scan rate: 100mV/s
Potential window (V): (-1.35, -0.5)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r_{Ni}: 5e-3 cm
α: 0.35
k^o : 3.5e-7 cm s^{-1}
C: 24 mM
E_f : -0.3506 V



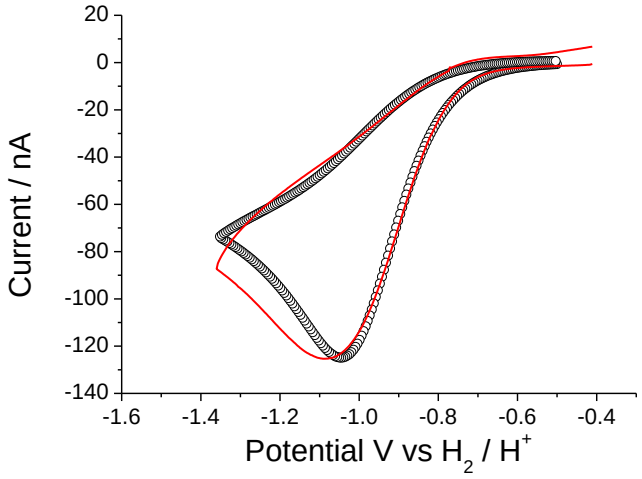
Ni
Scan rate: 200mV/s
Potential window (V): (-1.35, -0.5)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r_{Ni}: 5e-3 cm
α: 0.35
k^o : 3.5e-7 cm s^{-1}
C: 24 mM
E_f : -0.3506 V



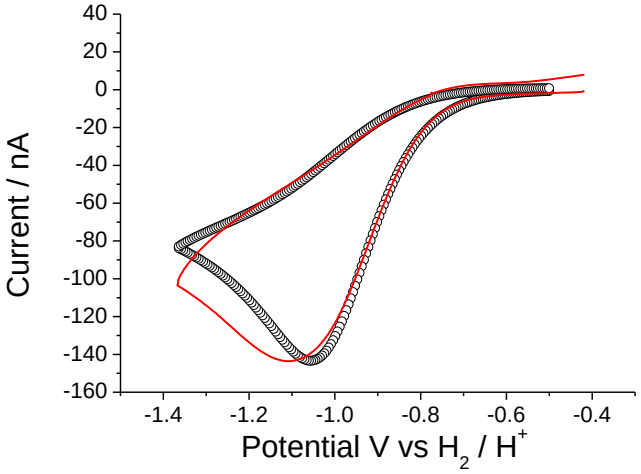
Ni
Scan rate: 400mV/s
Potential window (V): (-1.35, -0.5)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r_{Ni}: 5e-3 cm
α: 0.35
k^o : 3.5e-7 cm s^{-1}
C: 24 mM
E_f : -0.3506 V



Ni
Scan rate: 600mV/s
Potential window (V): (-1.35, -0.5)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Ni}$: 5e-3 cm
α: 0.35
k^o : 3.5e-7 cm s^{-1}
C: 24 mM
E_f : -0.3506 V

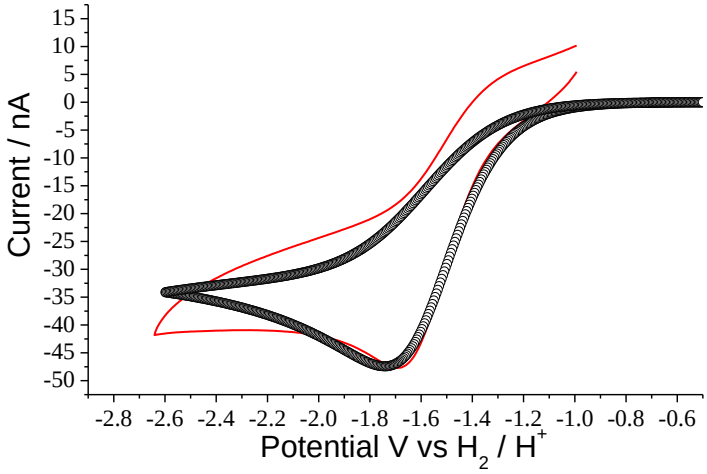


Ni
Scan rate: 800mV/s
Potential window (V): (-1.35, -0.5)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r $_{Ni}$: 5e-3 cm
α: 0.35
k^o : 3.5e-7 cm s^{-1}
C: 24 mM
E_f : -0.3506 V

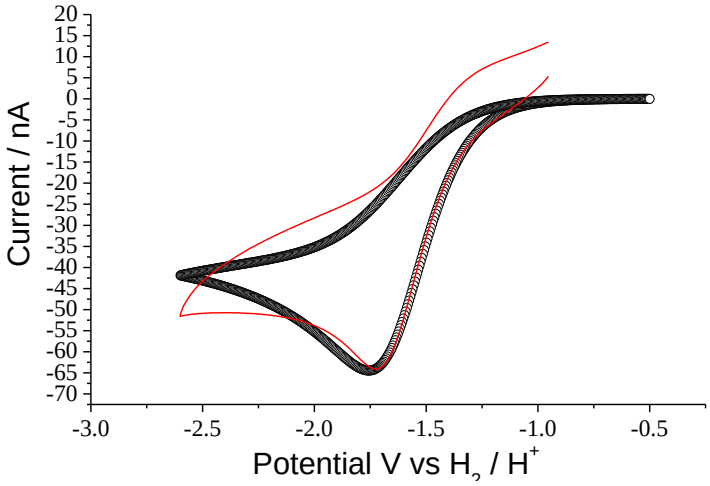


1.5. scan rate study of H[NTf$_2$] reduction on Titanium in [C$_2$mim][NTf$_2$])

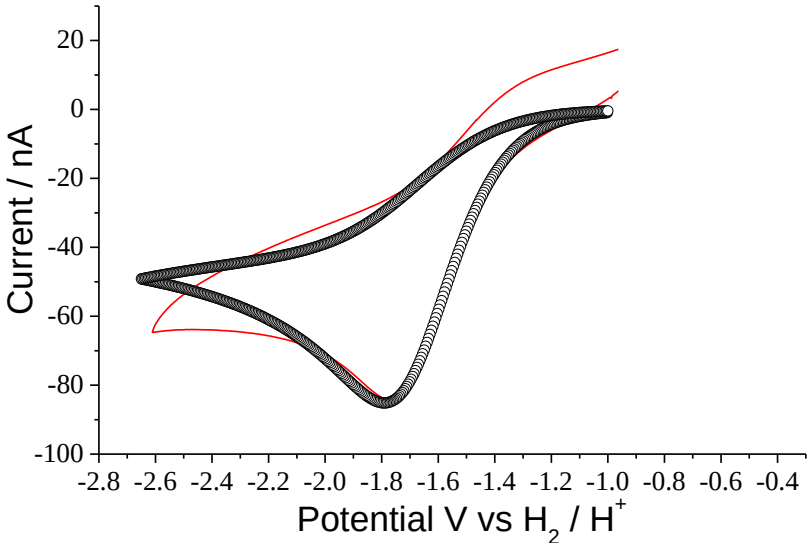
Ti
Scan rate: 100mV/s
Potential window (V): (-2.6, -0.6)
D (HNTf2): 2.5e-7 cm^{2}s^{-1}
D (H_2): 5.5e-6 cm^{2}s^{-1}
r $_{Ti}$: 2.5e-3 cm
α: 0.2
k^o : 3.5e-8 cm s^{-1}
C: 88 mM
E_f : -0.3506 V



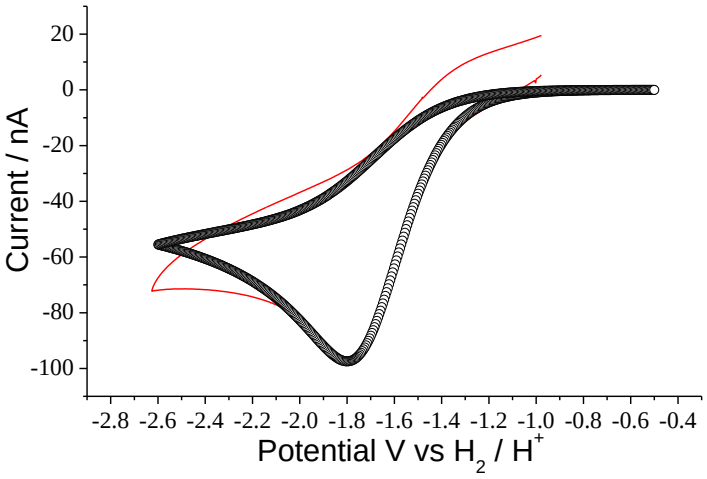
Ti
Scan rate: 200mV/s
Potential window (V): (-2.6, -0.6)
D (HNTf2): 2.5e-7 cm^{2}s^{-1}
D (H_2): 5.5e-6 cm^{2}s^{-1}
r $_{Ti}$: 2.5e-3 cm
α: 0.2
k^o : 3.5e-8 cm s^{-1}
C: 88 mM
E_f : -0.3506 V



Ti
Scan rate: 400mV/s
Potential window (V): (-2.6, -0.6)
D (HNTf2): 2.5e-7 cm^{2}s^{-1}
D (H_2): 5.5e-6 cm^{2}s^{-1}
r $_{Ti}$: 2.5e-3 cm
α: 0.2
k^o : 3.5e-8 cm s^{-1}
C: 88 mM
E_f : -0.3506 V



Ti
Scan rate: 600mV/s
Potential window (V): (-2.6, -0.6)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r_{Ti}: 2.5e-3 cm
α: 0.2
k^o : 3.5e-8 cm s^{-1}
C: 88 mM
E_f : -0.3506 V



Ti
Scan rate: 800mV/s
Potential window (V): (-2.6, -0.6)
D (HNTf2): 2.5e-7 cm^2s^{-1}
D (H_2): 5.5e-6 cm^2s^{-1}
r_{Ti}: 2.5e-3 cm
α: 0.2
k^o : 3.5e-8 cm s^{-1}
C: 88 mM
E_f : -0.3506 V