Supplemental information for:

The electrochemical behaviour of ferrocene in deep eutectic solvents based on quaternary ammonium and phosphonium salts

Laleh Bahadori[a], Ninie Suhana Abdul Manan[b], Mohammed Harun Chakrabarti[a,c], Mohd. Ali Hashim[a], Farouq Sabri Mjalli[d], Inas Muen AlNashef [e], Mohd. Azlan Hussain[a], Chee Tong John Low[f]

[a]*Department of Chemical Engineering, Faculty of Engineering, University of Malaya, Kuala Lumpur-50603, Malaysia*

[b]*Department of Chemistry, Faculty of Science, University of Malaya, Kuala Lumpur 50603, Malaysia*

[c]*Energy Futures Lab, Electrical Engineering Building, Imperial College London, South Kensington, London SW7 2AZ, UK*

[d]*Petroleum & Chemical Engineering Department, Sultan Qaboos University, Muscat 123, Oman*

[e]*Department of Chemical Engineering, College of Engineering, King Saud University, PO Box 800, Riyadh, Kingdom of Saudi Arabia*

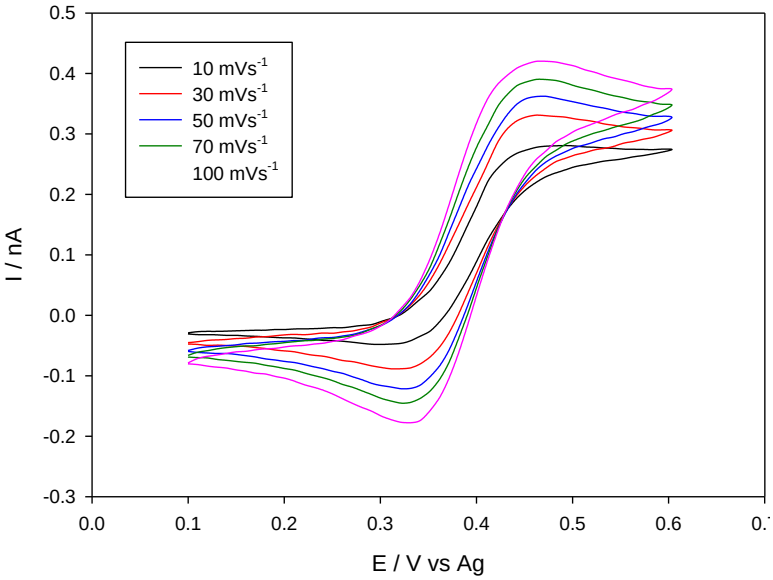
[f]*Electrochemical Engineering Laboratory, Energy Technology Research Group, Faculty of Engineering and the Environment, University of Southampton, Highfield, Southampton SO17 1BJ, UK*

Abstract

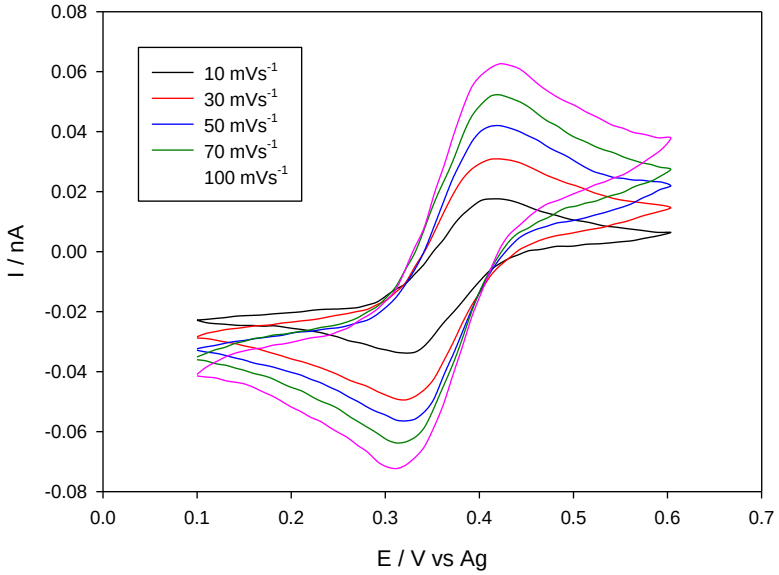
The electrochemical behaviour of ferrocene (Fc) is investigated in six different deep eutectic solvents (DESs) formed by means of hydrogen bonding between ammonium and phosphonium salts with glycerol and ethylene glycol. Combinations of cyclic voltammetry and chronoamperometry are employed to characterise the DESs. The reductive and oxidative potential limits are reported versus the Fc/Fc^+ couple. Diffusion coefficient, *D*, of ferrocene in all studied DESs is found to lie between 8.49×10^{-10} to 4.22×10^{-8} $cm^2\ s^{-1}$ (these do not change significantly with concentration). The standard rate constant for heterogeneous electron transfer

across the electrode/DES interface is determined to be in between 1.68×10^{-4} to 5.44×10^{-4} cm s^{-1} using cyclic voltammetry for the Fc/Fc^{+} couple in the DESs.

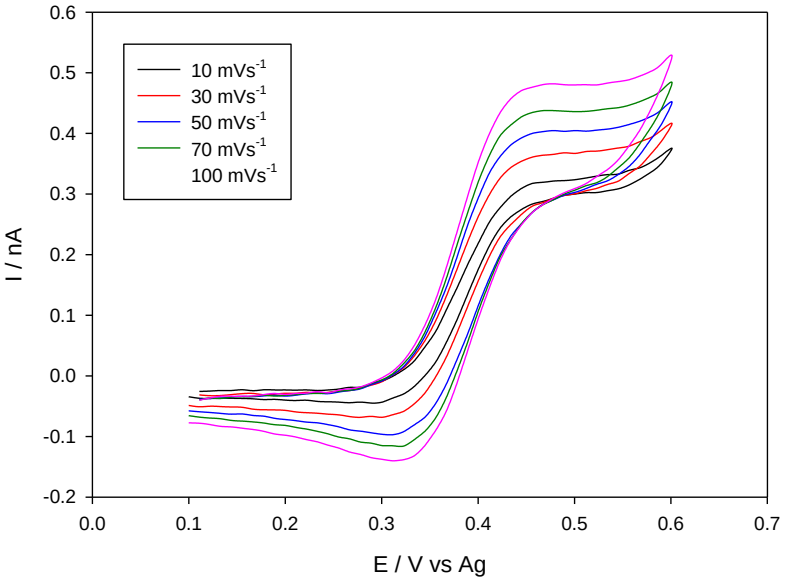
(a)


10 mVs-1
30 mVs-1
50 mVs-1
70 mVs-1
100 mVs-1
I / nA
E / V vs Ag

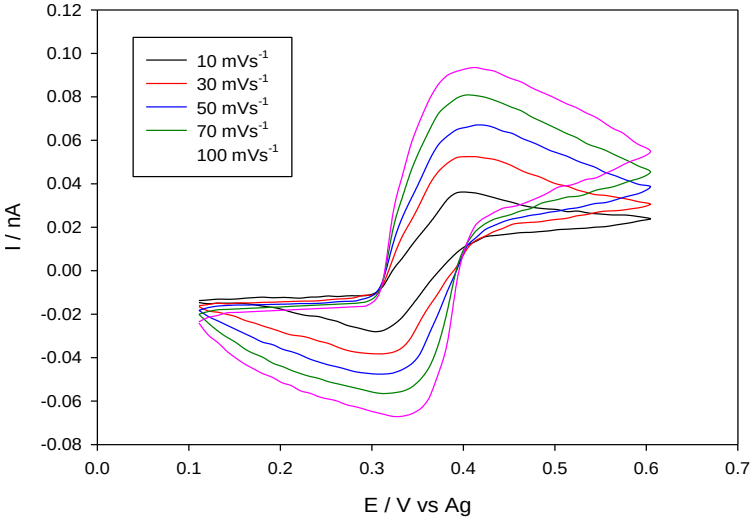
(b)


10 mVs-1
30 mVs-1
50 mVs-1
70 mVs-1
100 mVs-1
I / nA
E / V vs Ag

(c)


10 mVs-1
30 mVs-1
50 mVs-1
70 mVs-1
100 mVs-1
I / nA
E / V vs Ag

(d)


10 mVs-1
30 mVs-1
50 mVs-1
70 mVs-1
100 mVs-1
I / nA
E / V vs Ag

(e)

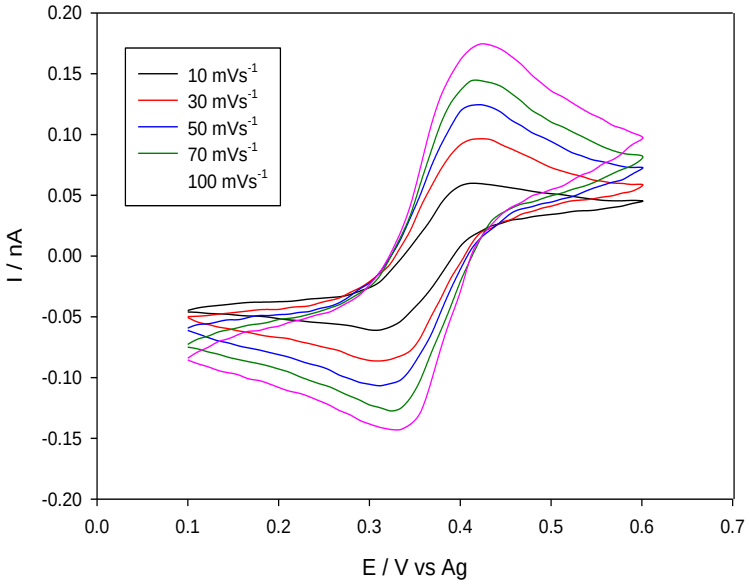
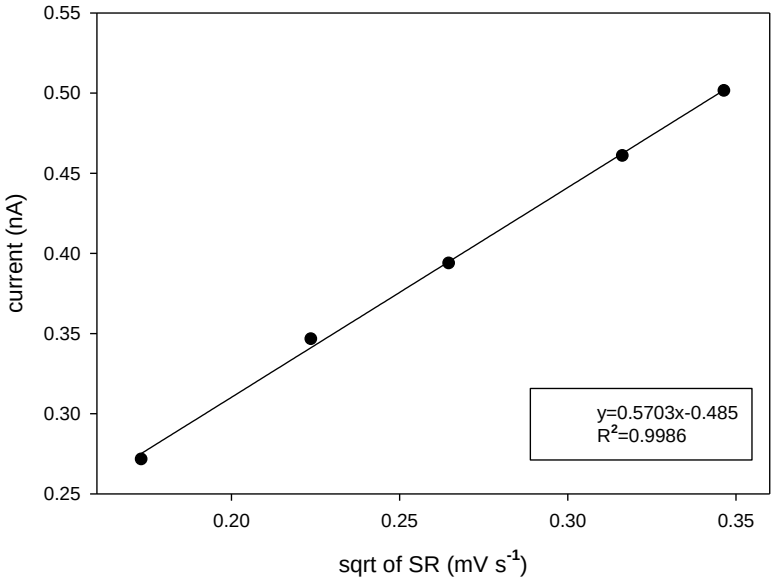
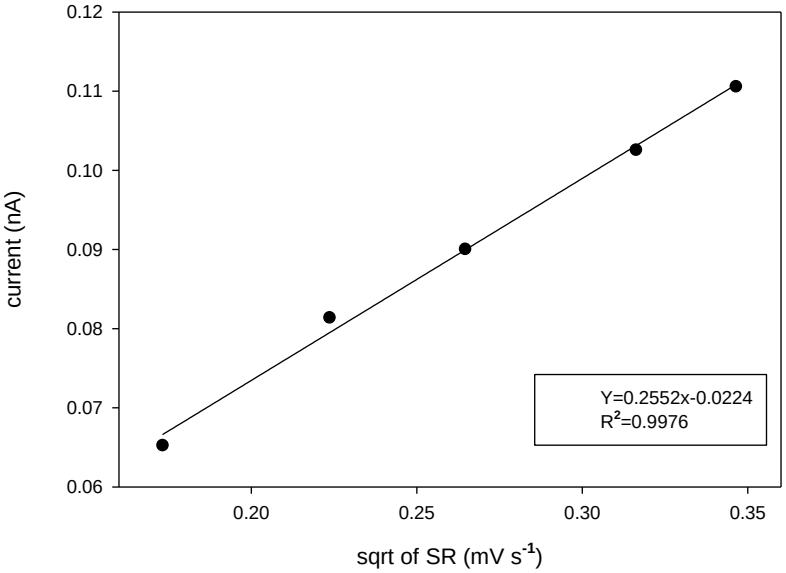


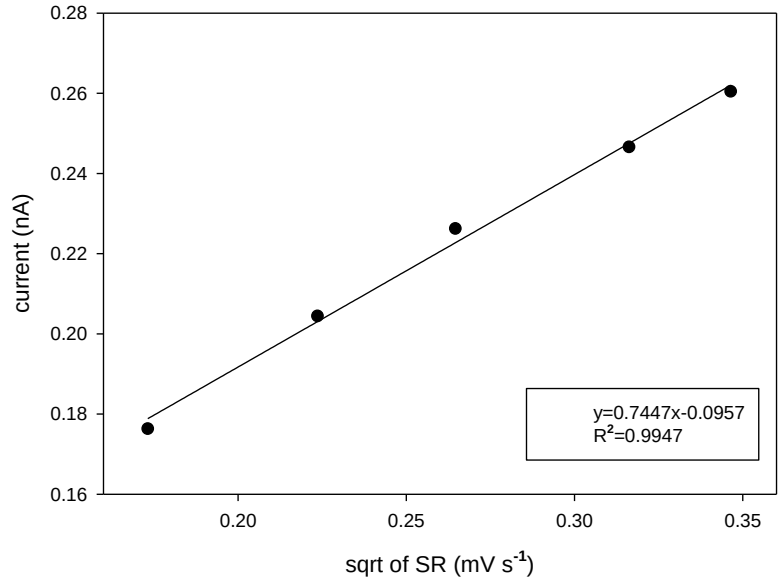
Figure S1. Cyclic voltammetry for the oxidation of 5.21mM ferrocene in (a) DES1, (b) DES2, (c) DES3, (d) DES4, (e) DES6 on a Pt electrode (diameter 20 µm) at varying scan rates of 10, 30, 50, 70 and 100 mV s^{-1} (from bottom to top).



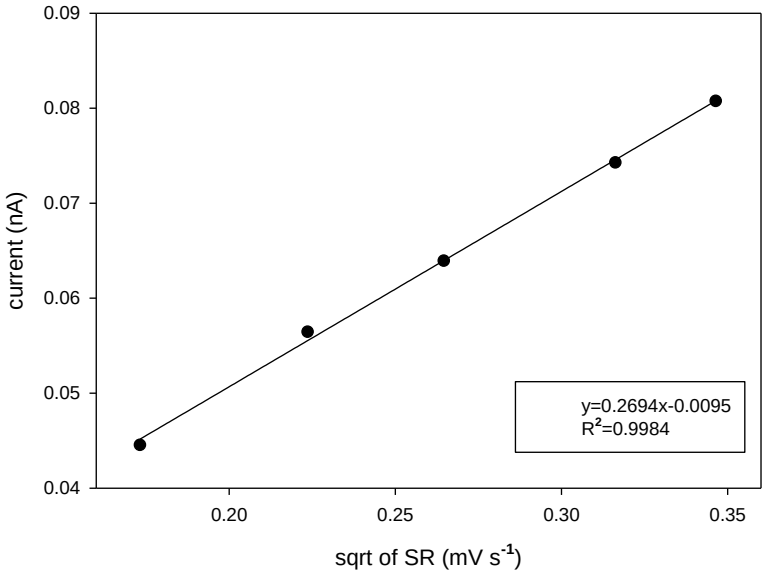
(a)



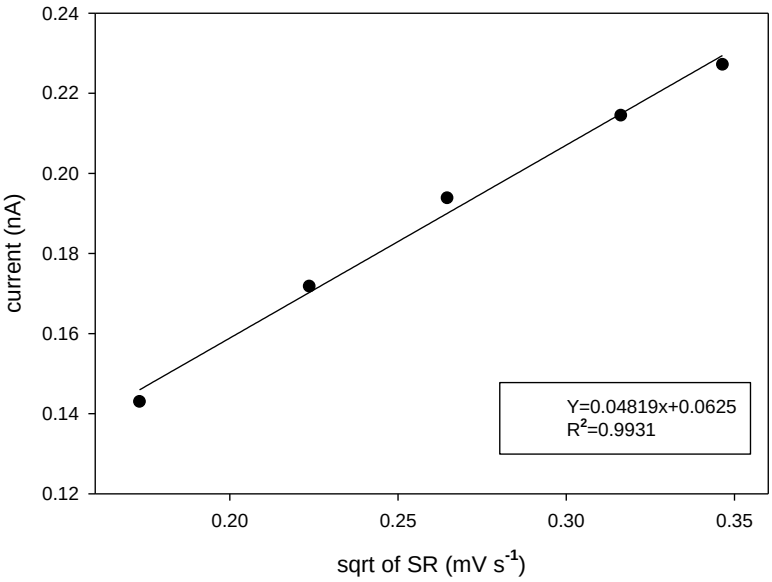
(b)



(c)

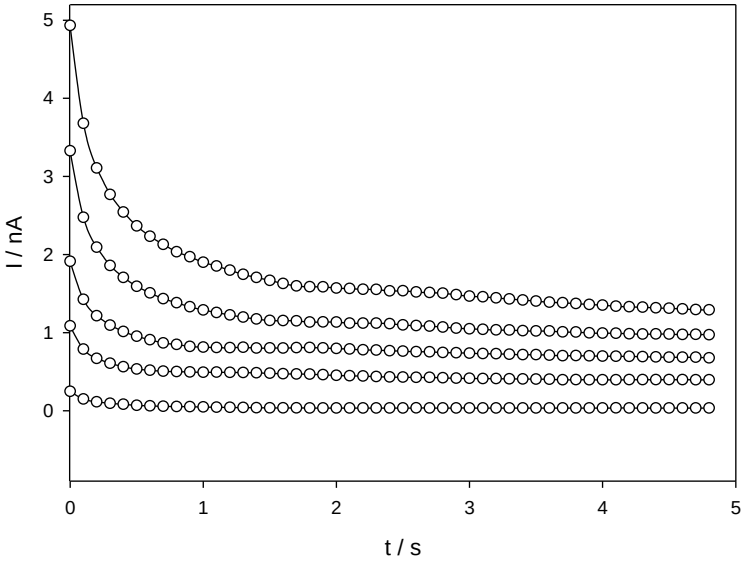


(d)

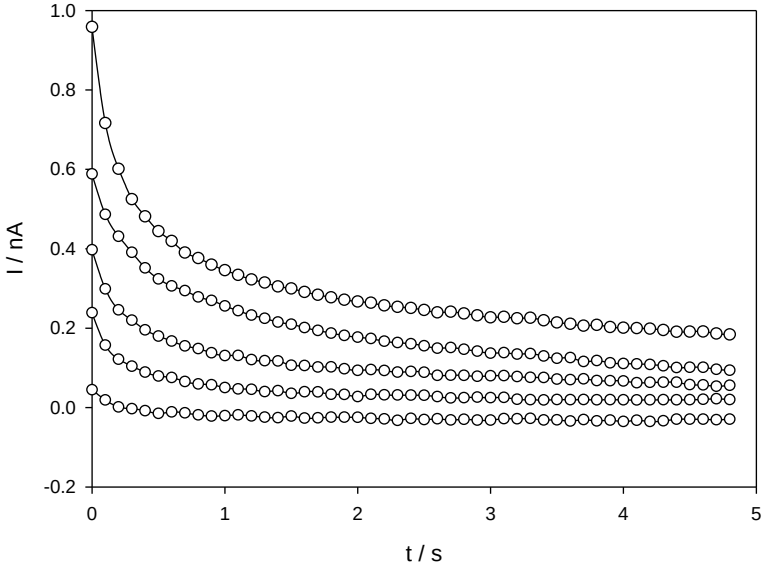


(e)

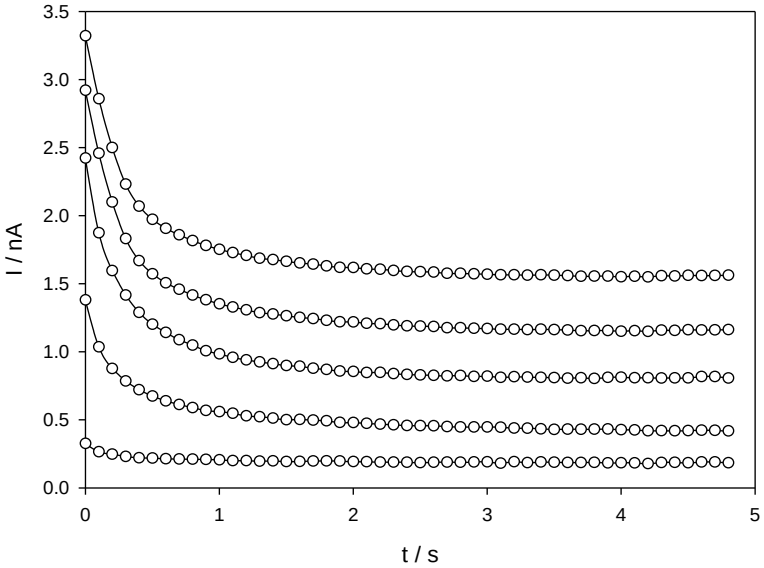
Figure S2.Linear dependence of peak current vs. square root of scan rates (SR) for Fc/Fc^+ using a Pt electrode in different DESs. Plots for 5.21mM solution of Fc in (a) DES1, (b) DES2, (c) DES3, (d) DES4 and (e) DES6 are clearly shown.


I / nA
t / s
0
1
2
3
4
5

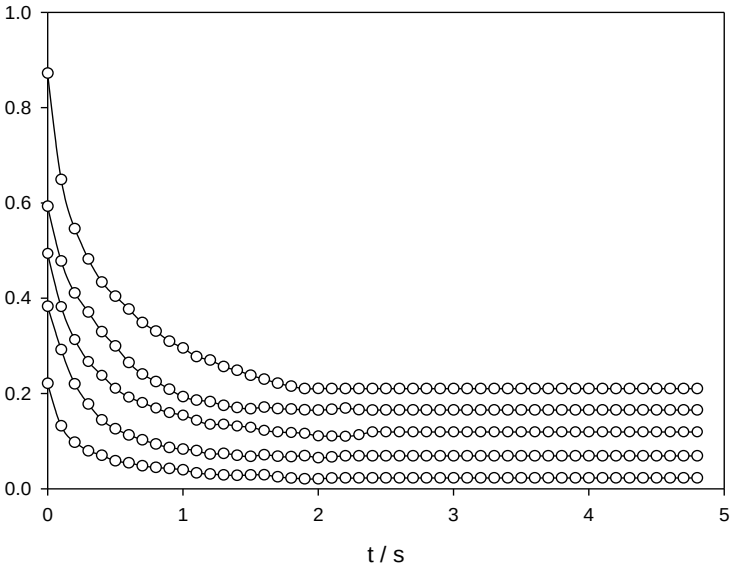
(a)


I / nA
t / s
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
0
1
2
3
4
5

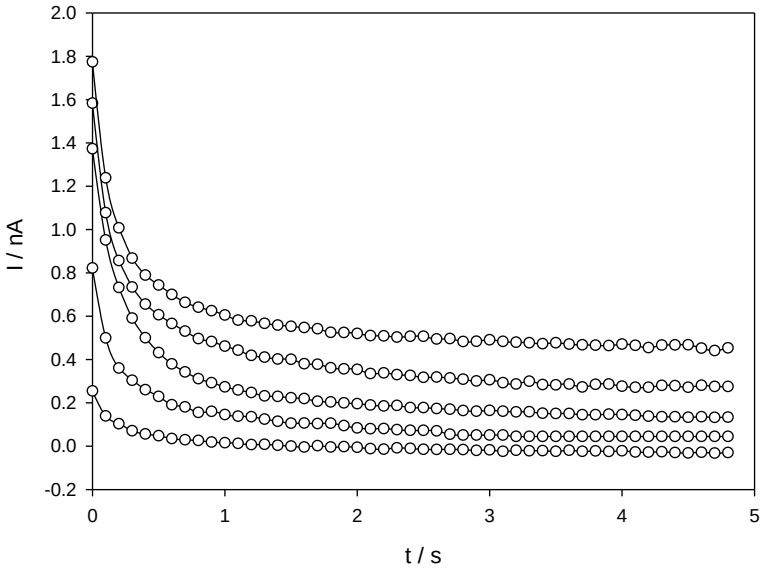
(b)


I / nA
t / s
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0
1
2
3
4
5

(c)


t / s
0.0
0.2
0.4
0.6
0.8
1.0
0
1
2
3
4
5

(d)



(e)

Figure S3. Experimental (—) and fitted theoretical (o) chronoamperometric transients for the oxidation of 1.08, 5.21,10 .13, 20.18 and 30.06 mM Fc in (a) DES1, (b) DES2, (c) DES3, (d) DES4 and (e) DES6 at a 20 μm Pt microelectrode.