QUEEN'S UNIVERSITY BELFAST

QUEEN'S UNIVERSITY IONIC LIQUID LABORATORIES

QUILL

Electro-photo generation of highly reducing radical anions for CO_2 activation

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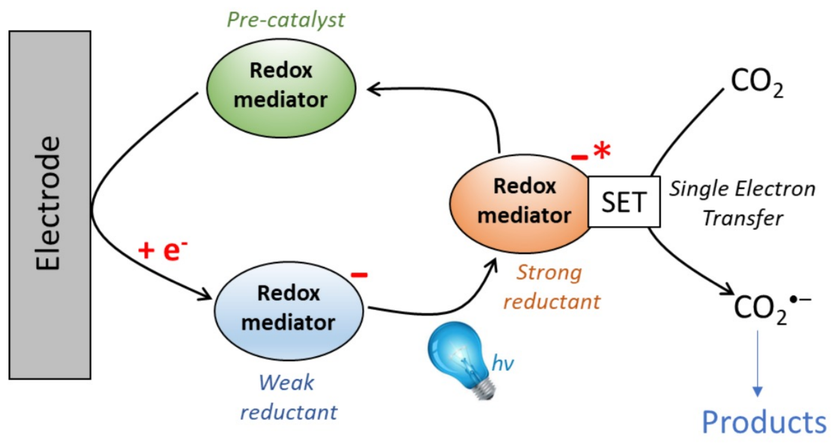
Electrophotochemistry



The catalyst is first oxidised or reduced at the electrode, then excited to a radical state using light.

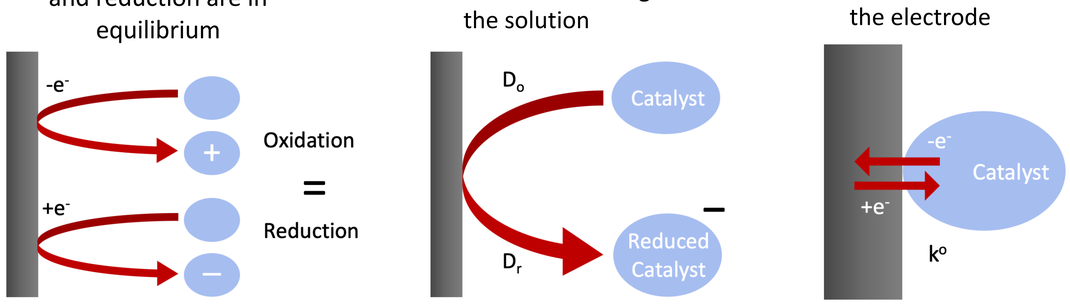
Electrochemistry Study

We wanted to accurately measure three electrochemical properties of a range of electrocatalysts:

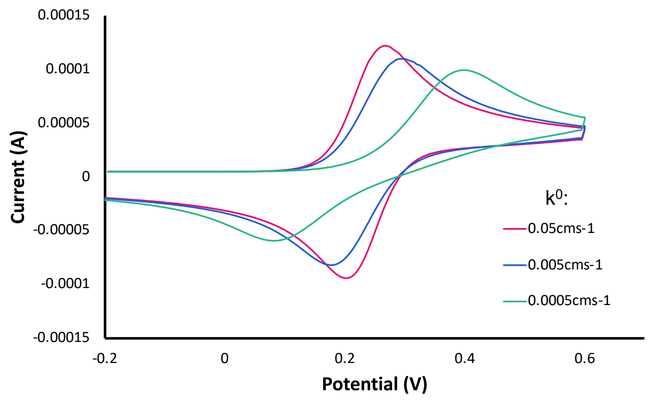
Redox potential (E^o)
electrochemical oxidation and reduction are in equilibrium

Diffusion co-efficient (D)
speed at which the substrate diffuses through the solution

Electron transfer constant (k^o)
speed at which electrons can transfer across the surface of the electrode



The k^o value is reported less frequently in papers, however it is very important as it represents the electrochemical reversibility of the catalyst. A high k^o means a more reversible catalyst.



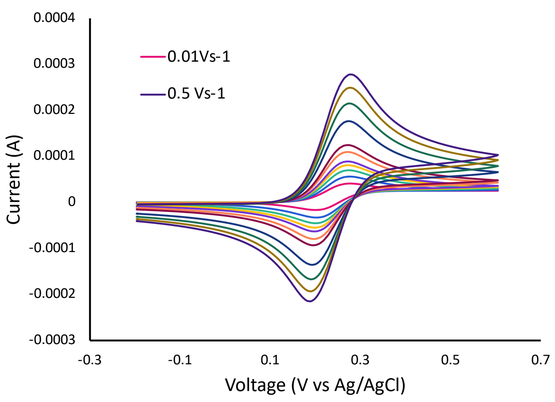
Randles-Sevcik equation:

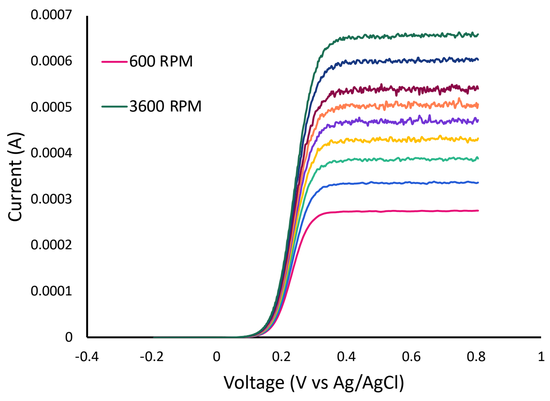
$$i_p = 0.4463\, nFAC\left(\frac{nFvD}{RT}\right)^{\frac{1}{2}}$$

$$D = \frac{(slope)^2}{n^3\,(2.69\times10^5\; A\; C^*)^2}$$

$$k^O = \frac{slope \times \left[\left[\left(\frac{nF}{RT}\right)\pi D_r\right]^{\frac{1}{2}}\right]}{\left(\frac{D_r}{D_o}\right)^{1/4}}$$

Previously, using the Randles-Sevcik equation on irreversible reactions provides inaccurate results as it assumes the reactions are reversible, therefore we turn to using the Nicholson method[1] with rotational disc voltammetry (RDV) to calculate reproducible and accurate values.

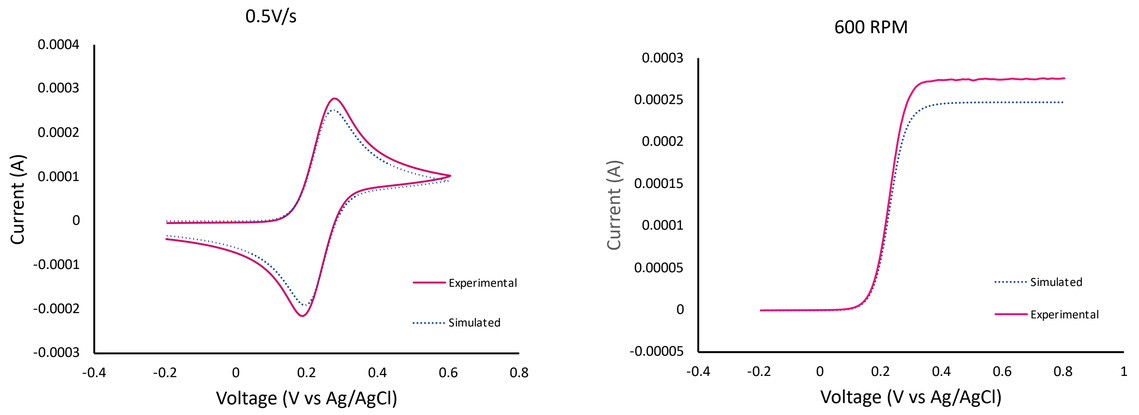




CV and RDV of TEMPO (5mM) in MeCN with TBAP electrolyte (150mM),

Electrophotocatalyst Results

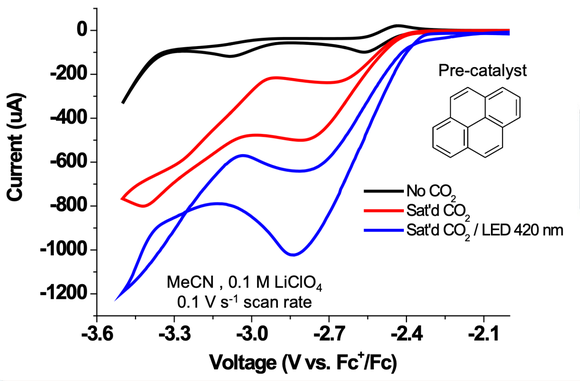
To confirm accuracy of the results, we used DigiSim software to simulate CV and RDV scans:

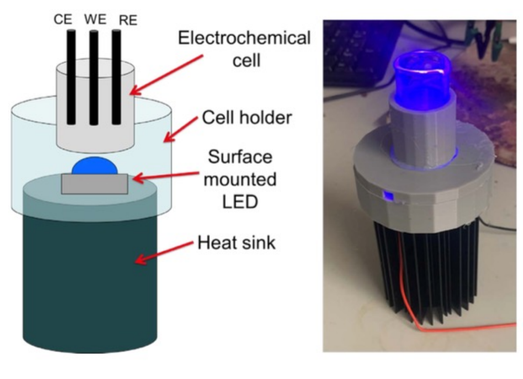


CV and RDV of TEMPO (5mM) in MeCN with TBAP electrolyte (150mM), at 0.5V/s, compared to simulated data.

Future Plans

Catalysts will be tested under UV light to observe their photoactivity. These are some preliminary results for reducing carbon dioxide using an electrophotocatalytic system.





Acknowledgements

Department for the Economy

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References:

1. Magno *et al*., Electroanalysis 2004, 16, 505. .
2. Moutet and Reverdy, *Chem. Commun*, 1982, 654–655.