Supplementary Information: Reduction of Carbon Dioxide in 1-Butyl-3-methylimidazolium Acetate

Short chronoamperometric transients (10 s) were achieved using a sample time of 0.01 s. The pre-treatment step consisted of holding the potential at 0 V for 20 s, followed by a 2 s equilibration period. The potential was stepped to the required value, and the current was measured for 10 s. Transients measuring the sustained reduction of CO_2 used an interval time of 0.2 s. The pre-treatment step was the same as in the short time scale experiments, but once the potential was stepped to the required value, the current was measured for 900 s.

The nonlinear curve fitting function in Origin 7.0 (MicroCal Software Inc.) following the Shoup and Szabo[1] approximation as employed by Evans *et al*.[2] was used to fit the experimental data. The equations used in this approximation describe the current response within an accuracy of 0.6% and are given below:

$$I = -4nFDcr_d f(\tau) \quad (1)$$

$$f(\tau) = 0.7854 + 0.8863\tau^{-1/2} + 0.2146e^{-0.7823\tau^{-1/2}} \quad (2)$$

$$\tau = \frac{4Dt}{r_d^2} \quad (3)$$

where n is the number of electrons transferred, F is the Faraday constant, D is the diffusion coefficient, c is the bulk concentration of parent species, r_d is the radius of the microdisk electrode, and t is the time.

The value of the electrode radius was fixed, having been previously electrochemically calibrated by analysing the steady state voltammetry of a 2 mM ferrocene solution in acetonitrile, which contained 0.1 M TBAP as a supporting electrolyte. The software performed up to one hundred iterations on the data, stopping when the experimental data had been optimised. A value for the diffusion coefficient, D, and the product of the number of electrons and the concentration of the parent species, nc, was thus obtained.

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[1] D. Shoup and A. Szabo, *J. Electroanal. Chem.* 1982, **140**, 237.
[2] R. G. Evans, O. V. Klymenko, S. A. Saddoughi, C. Hardacre and R. G. Compton, *J. Phys. Chem. B.* 2004, **108**, 7878.