Supporting Information for

Using chronoamperometry to rapidly measure and quantitatively analyse rate-performance in battery electrodes

Ruiyuan Tian,1,2 Paul J. King,3 Joao Coelho,2,4 Sang-Hoon Park,2,4 Dominik V Horvath,1,2 Valeria Nicolosi,2,4 Colm O’Dwyer,2,5 Jonathan N Coleman1,2\*

*1School of Physics, Trinity College Dublin, Dublin 2, Ireland*

*2AMBER Research Center, Trinity College Dublin, Dublin 2, Ireland*

*3Efficient Energy Transfer Department, Bell Labs Research, Nokia, Blanchardstown Business & Technology Park, Snugborough Road, Fingal, Dublin 15, Ireland*

*4School of Chemistry, Trinity College Dublin, Dublin 2, Ireland*

*5 School of Chemistry, University College Cork, Tyndall National Institute, and Environmental Research Institute, Cork T12 YN60, Ireland*

\*colemaj@tcd.ie (Jonathan N. Coleman); Tel: +353 (0) 1 8963859.

Using high rate approximations to capacity rate equations to ensure consistency between characteristic times.

The following equation has been reported by Tian et al.

 (16, Tian et al)

Taylor expanding this equation and taking the first 3 terms allows us to generate an approximate equation which described the high rate portion:



Tian et al used this equation to fit literature data to generate a database of ~200 τ-values for a range of materials. Because this database is quite useful, we want to make sure that if other equations are used to fit Q/M v R data, they output fit constants that are consistent with Tian’s. The simplest way to ensure this is to make sure that other equations are written in such a way that their high rate approximation matches that above.

Heubner et al proposed an equation for Q/M in terms of C-rate. However, in the main text, we show that this equation is more suited to fitting Q/M vs. R data. Thus, we reproduce the equation here in terms of R, rather than C-rate:

 (17, Heubner et al)

Taylor expanding this equation and taking the first 2 terms yields the high rate approximation:



This equation clearly does not match the high rate approximation to Tian’s equation and so will not output values of τ matching that of Tian.

However, if we rewrite this equation very slightly, adding a factor of 0.5:



The Taylor expansion gives the high rate approximation which matches Tian’s:



Similarly, the equation derived by us (eq 12):



Has a high rate approximation when Rτ>>1 and so:



Again, this doesn’t match Tian’s high-rate approximation. However, if we modify the equation:



The high-rate approximation becomes identical to Tian’s:





Figure S1: Comparison of results obtained by fitting Q/M vs. R data obtained by GCD measurements (left column) versus CA measurements (right column). We performed fits using three different equations: equation (13) obtained in this work (top row), Tian’s equation (middle row) and Heubner’s equation (bottom row). Fit parameters and a goodness-of-fit parameter are given in each panel.



Figure S2: Comparison of results obtained by fitting Q/M vs. C-rate data obtained by GCD measurements (left column) versus CA measurements (right column). We performed fits using two different equations: equation (13) obtained in this work (top row), and Wong’s equation (bottom row). Fit parameters and a goodness-of-fit parameter are given in each panel.



Figure S3: Comparison of τ and n fit parameters found 4 different ways: fitting Q/M versus either R or C-rate, with Q/M measured via GCD or CA measurements. Each material is colour coded as shown in the legend. Each measurement/fit type is coded via the symbol shape. In the ideal case, for a given material the fit parameter values would be very similar for each of the 4 sets of fit parameters and so data points of a given colour should be closely clustered. This is largely the case with the exception of the stars which are always separated from the other symbols of a given colour. This means the Q/M data measured by GCD and plotted versus C-rate fives fit parameters which are not perfectly consistent with the other values.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| M/A  (mg/cm2) | LE  (μm) | ρE  (g/cm3) | QM,1  (mAh/g) | τ1  (s) | n1 | QM,2  (mAh/g) | τ2  (s) | n2 |
| 8.79 | 24 | 3.2 | 192.1 | 154.9 | 1.04 | 3.46 | 0.48 | 1.11 |
| 10.2 | 28 | 3.2 | 187.7 | 157.2 | 0.93 | 1.90 | 0.52 | 1.08 |
| 10.1 | 28 | 3.2 | 178.0 | 140.0 | 1.30 | 7.20 | 1.19 | 1.05 |
| 12.3 | 34 | 3.2 | 161.8 | 169.9 | 1.19 | 5.15 | 1.38 | 1.25 |
| 16.3 | 45 | 3.2 | 188.8 | 275.3 | 0.92 | 1.75 | 0.51 | 1.16 |
| 20.9 | 58 | 3.2 | 186.5 | 444.9 | 1.03 | 6.04 | 2.87 | 0.99 |
| 26.5 | 74 | 3.2 | 183.0 | 448.1 | 0.94 | 2.36 | 1.69 | 1.01 |
| 30.4 | 84 | 3.2 | 180.9 | 743.3 | 0.95 | 2.69 | 1.47 | 1.14 |
| 39.6 | 110 | 3.2 | 179.7 | 946.4 | 0.99 | 3.88 | 4.05 | 1.00 |
| 41.3 | 117 | 3.1 | 189.3 | 2001.6 | 0.94 | 3.88 | 5.98 | 1.04 |
| 43 | 119 | 3.2 | 186.4 | 1481.6 | 1.02 | 5.50 | 7.61 | 1.00 |
| 43.5 | 120 | 3.2 | 188.8 | 1882.8 | 1.01 | 5.36 | 9.07 | 0.93 |

Table S1: Table 3: Electrode properties and fit parameters found by fitting the Q/M v R data for NCA/SWNT (0.5%) electrodes using equation 20.



Figure S4: Further analysis of CV data. A) Position of CV reduction peak as a function of scan rate. The line is a fit to:1



where α is the charge transfer coefficient and ν is the scan rate, and is consistent with α=0.35. This equation describes the peak shift in irreversible systems. Behaviour consistent with this equation continues up until a scan rate of ~10 mV before transitioning to a new behaviour at higher potential. The transition point is very similar to the scan rate where the high rate feature in the capacity-rate curves appears. The inset reproduces figure 5A.

B) Stored charge normalised to mass found by integrating under the CV curve ( where M is the electrode mass and ν is the scan rate). At just above 10 mV/s, the data transitions into  dependence (line) which is consistent with electrically limited behaviour. This is consistent with the data described in the main text.

1 Bard, A. J. & Faulkner, L. R. *Electrochemical methods: fundamentals and applications*. (John Wiley and sons, 2001).