##### **Supplementary material for “Reduced order model for a lithium ion cell with uniform reaction rate approximation”**

**S1. Numerical test of uniform reaction rate approximation**

The uniform reaction rate approximation implies a linear solid current profile in the electrodes i.e. the solid current density linearly varies from the total current density at the collector end to zero at the separator end. Hence, a test of the solid current linearity is a test of uniform reaction rate approximation. The solid currents in the two electrodes at 1C and 7C constant current discharges for a typical lithium ion cell with design and model parameters as in Section S4 are given in Figures S1 to S4. Over long times, the solid currents are reasonably linear. The nonlinear behavior of the solid currents will get accounted for in the reduced order model development with spatially varying reaction rate.

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**Figure S1: Spatial variation of solid current in negative electrode at different times (in seconds) during 1C discharge in the detailed electrochemical model.**

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**Figure S2: Spatial variation of solid current in positive electrode at different times (in seconds) during 1C discharge in the detailed electrochemical model.**

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**Figure S3: Spatial variation of solid current in negative electrode at different times (in seconds) during 7C discharge in the detailed electrochemical model.**

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**Figure S4: Spatial variation of solid current in positive electrode at different times (in seconds) during 7C discharge in the detailed electrochemical model.**

**S2. Migration current continuity across the interfaces:**

At the negative electrode – separator interface, the solid current goes to zero according to the boundary condition (3). Then, evaluating the negative electrode region total current balance (85) at that interface gives

 (S1)

Note that the electrolyte potential gradient, electrolyte concentration and its gradient at the interface can be written in terms of the interfacial migration current (88), interfacial concentration (26) and interfacial flux (27). Using these interfacial variables in equation (S1) and rearranging gives

 (S2)

Now, consider the negative electrode – separator interface from the separator side. Evaluating the separator total current balance (89) at that interface, using the interfacial variables as above, gives

 (S3)

Comparing equations (S2) and (S3), with concentration and flux continuities across the interface, migration current continuity requires that

 (S4)

Analyzing the separator – positive electrode interface similarly gives

 (S5)

Thus, the equality of the ratio of ionic conductivity and ionic diffusivity across the three regions

 (S6)

ensures migration current continuities at the electrode – separator interfaces. Note that the ionic conductivies and diffusivities appearing in the above equation are effective properties in a porous media i.e. they have Bruggeman factors as in equation (100). The condition (S5) requires that the Bruggeman factors for ionic conductivity and ionic diffusivity are identical, so that their ratio is independent of the porous matrix properties and is purely an electrolyte property. Since electrolyte is a single continuous phase between the two collector plates, it is obvious that electrolyte properties are continuous across the three regions.

**S3. Solid phase mass balance - Parabolic approximation**

Equation (124) shows that the volume average of the spherical diffusive flux is

 (124)

From this equation, the lowest order volume average respecting profile approximation is obtained as  (S7)

Rearranging the above equation and integrating it once with respect to *r* gives

 (S8)

where *f(t)* is some arbitrary function. From the symmetry boundary condition (120) it is easily seen that *f(t)* is zero. Then, rearranging gives

 (S9)

Note that equation (S9) satisfies the surface boundary condition (119). Integrating equation (S9) again with respect to *r* gives

 (S10)

where *f(t)* is some arbitrary function. Surface concentrations feed into Butler – Volmer kinetics, in the Section 6. Applying the surface concentration gives

 (S11)

Eliminating *f(t)* between equations (S10) and (S11) gives the parabolic concentration profile  (S12)

From the sphere volume average definition (122), the volume average of r2 is obtained as

 (135)

Using this result, sphere volume averaging equation (S12) and simplifying gives

 (S13)

Under the uniform reaction rate approximation, , all spheres have the same surface boundary condition (119). Since all the spheres have identical initial condition, and identical surface boundary condition, all of them evolve identically. Then the surface concentrations of these spheres are

 (S14)

It is known that during a high current charge or discharge, parabolic approximation fails, warranting a quartic approximation.

**S4. Cell design and model parameters for a typical lithium ion cell**

For the negative electrode (MCMB Carbon) the following open ciruit potential fuctional fit reported in Ref. [5] is used:

*Un* = 0.13966 + 0.68920 exp(− 49.20361 *SOCn*) + 0.41903 exp(− 254.40067 *SOCn*)

− exp(49.97886 *SOCn* − 43.37888) − 0.028221 *arctan*(22.52300 *SOCn* − 3.65328)

− 0.01308 *arctan*(28.34801 *SOCn* − 13.43960), (S15)

where the negative electrode state of charge is defined as

*SOCn = csn / csmaxn*. (S16)

For the positive electrode (A composite of lithium manganese, nickel and cobalt oxides) the depth of discharge is defined as

*DoD = (SOCp-SOCpmin)/( SOCpmax - SOCpmin)*, (S17)

where *SOCpmin* = 0.615617983, *SOCpmax* = 1 and

*SOCp = csp / csmaxp*. (S18)

The positive electrode open circuit potential is expressed in terms of this depth of discharge as

*Up* = 4.2344 - 9.1296 *DoD*6 + 25.8028 *DoD*5 - 26.0238 *DoD*4 + 11.1602 *DoD*3 - 1.9671 *DoD*2 - 0.2934 *DoD* (S19)

The positive electrode open circuit potential presented above is from an unpublished internal work of Wenbin Gu. The rest of the parameters listed below were collated by Kamakshi Jagannathan from literature and internal data. The author is thankful to both of them for these inputs. The notation is as in the main article.

