Corrigendum to Generalised single particle models for high-rate operation of graded lithium-ion electrodes: Systematic derivation and validation Electrochimica Acta 339 (2020) 135862

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In Figure 9 of [1], a comparison of the terminal voltage predicted by the SPMe from [2], DFN, SP, and cSP models is presented. In this figure, the SPMe appears to perform poorly at high C-rates. However, there is an implementation error in the code used to generate the figure, which results in an overprediction of the reaction overpotential in the SPMe.

The error is in the evaluation of the reaction current density j, which is defined in [1] as

$$j = 2Fkc^{1/2}(c_s)^{1/2}(c_s^{\max} - c_s)^{1/2} \sinh\left(\frac{F\eta}{2R_gT}\right), \tag{1}$$

but in [2] as

$$j = mc^{1/2}(c_s)^{1/2}(c_s^{\max} - c_s)^{1/2} \sinh\left(\frac{F\eta}{2R_gT}\right), \tag{2}$$

so that the reaction rate constants are related by $m = 2Fk$. The factor of 2 was erroneously omitted in the calculations of [1]. Figure 1 shows the corrected comparison.

We make one further comment on the results. In [2], the SPMe is formally derived in the limit of fast diffusion in the electrolyte, with no *ad-hoc* assumptions. This results in a linear diffusion equation (with a piecewise-constant source term s^0) for the electrolyte concentration of the form

$$\varepsilon\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D(c^0)\frac{\partial c}{\partial x}\right) + s^0, \qquad \text{(Linear)}. \tag{3}$$

During the discussion in [2] it is suggested that, although it includes formally higher-order terms in the asymptotic expansion, including nonlinear electrolyte diffusion,

$$\varepsilon\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D(c)\frac{\partial c}{\partial x}\right) + s^0, \qquad \text{(Nonlinear)}, \tag{4}$$

may in some situations give better results in practice. The example in [1] in which $D(c)$ varies by an order of magnitude, with a discharge rate of 7.5C, is one such situation.

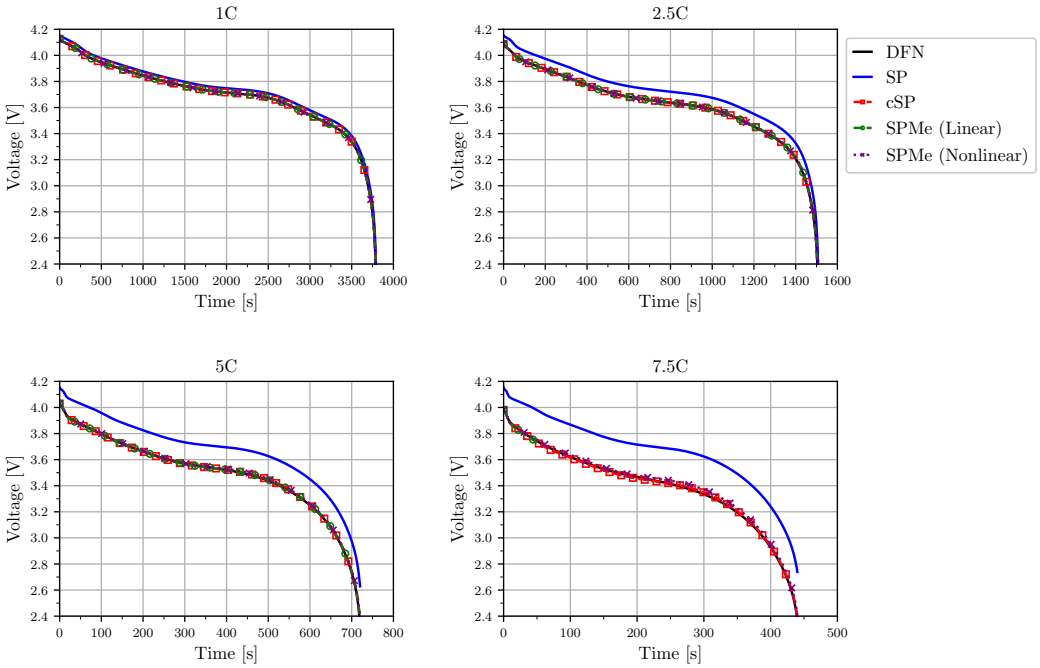

Figure 1: Comparison between the DFN model, the SPM, the cSP [1], and the SPMe [2] at different discharge rates. Results for the SPMe with both linear and nonlinear diffusion in the electrolyte are included.

At a discharge rate of 7.5C the SPMe (Linear) predicts that the electrolyte concentration goes negative close to the current collector at around 40s. At this point, the linear model is operating outside of its range of validity, and gives results that are non-physical (we therefore terminate the simulation of the SPMe (Linear) at 40s in Fig. 1). This non-physical behaviour is remedied if the linear diffusion (3) is switched to the nonlinear diffusion (4). Then, even at 7.5C, both the SPMe (Nonlinear) [2] and the cSP [1] accurately recover the terminal voltage as predicted by the DFN (see Figs. 1 and 2, and Table 1).

The code to produce the results shown is available at `https://github.com/rtimms/spme-comparison`.

	RMSE (mV)			
	1C	2.5C	5C	7.5C
SPM	36.42	92.03	181.3	270.2
SPMe (Linear)	0.6898	2.767	5.109	-
SPMe (Nonlinear)	0.7012	3.101	7.873	21.11
CSP	0.8403	3.2964	5.6469	9.9202

Table 1: Root-mean square error (RMSE) for each reduced-order model compared to the DFN at different C-rates. Note that the error for the linear SPMe at 7.5C is omitted as the model breaks down before the discharge is complete.

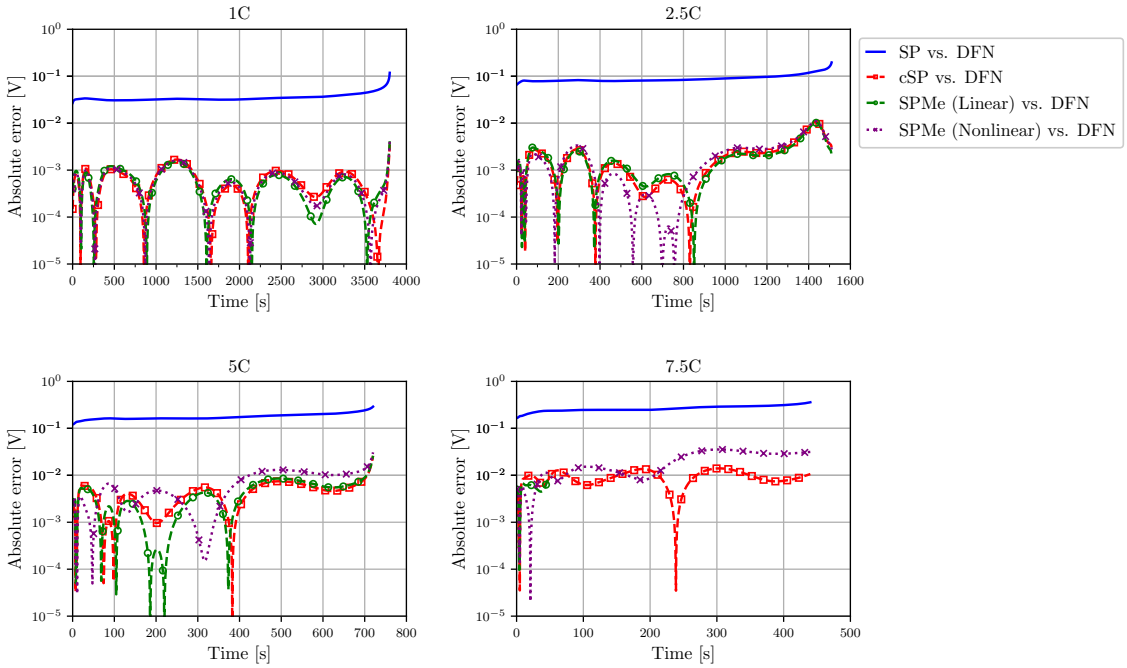

Figure 2: Absolute errors of the SPM, the cSP [1], and the SPMe [2] vs. the DFN at different discharge rates. Results for the SPMe with both linear and nonlinear diffusion in the electrolyte are included.

References

[1] G. Richardson, I. Korotkin, R. Ranom, M. Castle, and J.M. Foster. Generalised single particle models for high-rate operation of graded lithium-ion electrodes: Systematic derivation and validation. *Electrochimica Acta*, 339:135862, 2020.

[2] S.G. Marquis, V. Sulzer, R. Timms, C.P. Please, and S.J. Chapman. An Asymptotic Derivation of a Single Particle Model with Electrolyte. *Journal of The Electrochemical Society*, 166(15):A3693–A3706, 2019.