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# Effect of Solvent Segregation on the Performance of Lithium-Ion Batteries

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## Abstract

The pseudo two-dimensional (P2D) model is one of the most powerful tools in modelling lithium-ion batteries (LIBs) <sup>1</sup>, in that it can describe the complex electrochemical and thermal behaviours of LIBs with high fidelity yet maintain relatively high computing efficiency. To achieve that, many assumptions have been made, one of which is the single solvent assumption. However, most electrolytes used in LIBs uses multiple solvents to balance the requirements of conductivity, diffusivity and viscosity <sup>2</sup>. Therefore, the single solvent assumption indicates that all solvents move as a single entity.

However, previous experimental studies have shown that  $\text{Li}^+$  preferentially attracts cyclic carbonates (like ethylene carbonate, EC) rather than linear carbonates (such as ethyl-methyl carbonate, EMC) to form ion-solvent clusters<sup>3</sup>. During charge/discharge, ion-solvent clusters move between the positive and negative electrodes to constitute ionic current. At the electrolyte-electrolyte interface,  $\text{Li}^+$  de-solvates from the clusters and intercalates into the electrode, or vice versa. Such process will induce concentration gradients of both solvents and lithium ions; the solvent concentration has been ignored in the P2D model. The simplification means the current P2D model fails to capture two important phenomena: (1) many electrolyte properties - including conductivity, diffusivity, and thermodynamic factors - are sensitive to the solvent concentration<sup>4</sup>; (2) the solvent components in the ion-solvent clusters are preferentially consumed by interfacial side reactions such as the growth of solid-electrolyte interface (SEI)<sup>3</sup>.

To fill this gap, we add an extra governing equation for the solvent concentration (in our case, EC) which allows us to describe an electrolyte with two solvents and one salt. We also include a cross diffusion term to consider the dragging effect between the working solvent (EC) and lithium ions. For the charge conservation equation, we directly use measured liquid junction potential as a function of both solvent and lithium-ion concentration, which avoids possible errors brought by identifying the thermodynamic factors.

To elucidate the effect of solvent segregation, we compare the overpotential and concentration profile of Li ion and EC at the end of 3C discharge of the normal DFN (single case) and our revised model (double case). The revised model predicts opposite EC concentration compared with  $\text{Li}^+$ , which has been observed by Wang et al.<sup>5</sup> For a high value of  $\alpha$ , the dragging effect between  $\text{Li}^+$  and EC is more significant, inducing high concentration gradients of both species. The EC overpotential can be as high as 10 mV and further affects the rate performance of LIBs. This revised model captures more complicated transport mechanisms in the electrolyte and opens the chance of linking the microscopic understanding on solvation structure to a continuum level model.

## Reference:

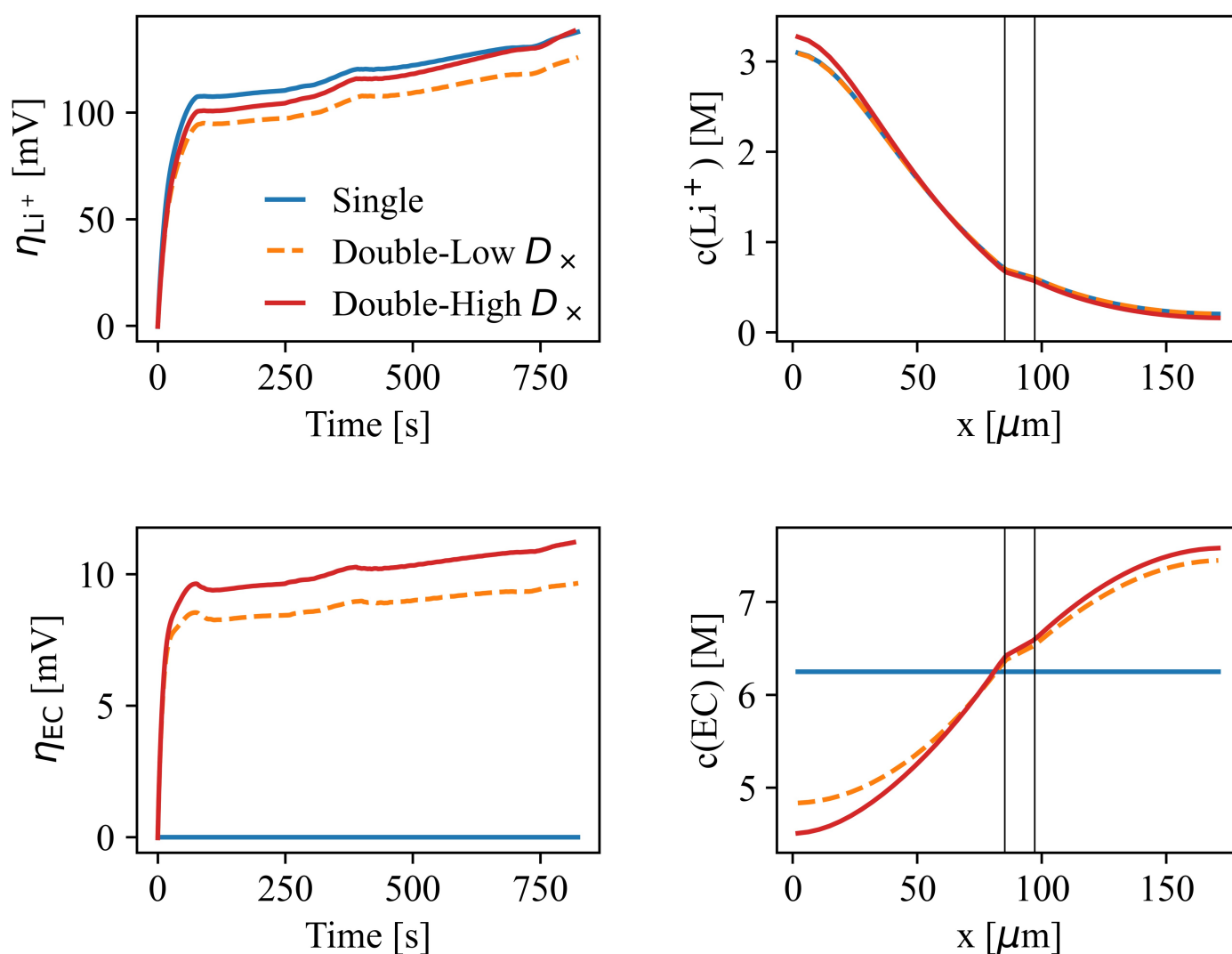
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