Revealing species distribution and morphology of SEI formation using kinetic Monte Carlo

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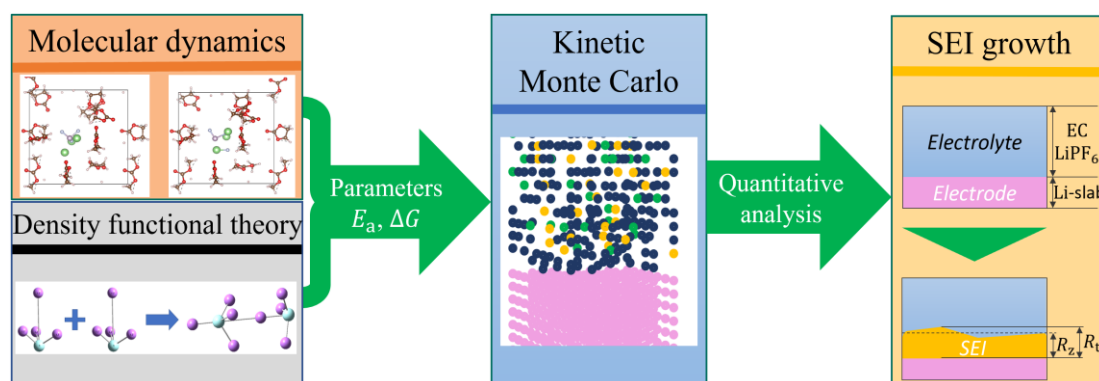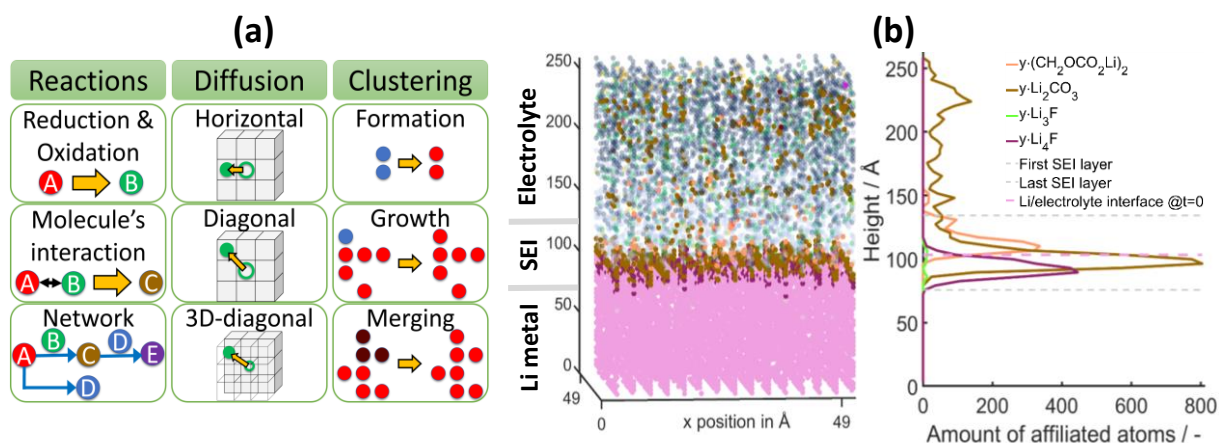*Email address: gerasimov @kit.edu

Figure 1: Flow chart of SEI growth model

Secondary lithium metal batteries are one of the promising technologies for future energy storage, even though the technology still faces issues regarding safety. One challenge is the generation of a stable and well performing Solid-Electrolyte Interphase (SEI) which is a layer containing several species produced by (electro-)chemical reactions between lithium metal and electrolyte. The SEI enhances the battery's safety by protecting the surface from further direct contact with electrolyte but also decreases its performance due to irreversible lithium consumption [1]. Although much research has been performed to unravel the SEI formation mechanism and structure, it is still not fully understood. Through understanding the complex interaction of reactions at the surface, strategies for manipulating the formation of the SEI could be developed that aid to reduce the performance losses while maintaining the SEIs protective traits.

Thus, this study aims to reveal the evolution of the internal species distribution and geometrical aspects of the native SEI formation by model-based analysis. Both properties determine the performance of the SEI and its electrical resistance or mechanical properties. To achieve this, a combination of molecular dynamics/density functional theory (MD/DFT) and kinetic Monte Carlo (KMC) simulations is used (Figure 1). Thereby, MD/DFT provides chemical parameters needed for the KMC simulation which finally determines the SEI growth features. This is done by implementing reactions, diffusion, and clustering as well as the corresponding large set of species as stochastic processes in MATLAB (Figure 2a).

The results of the simulations suggest a layered SEI species structure from an $EC/LiPF_6$ ($2\,M$) electrolyte, whereby at the lithium interface LiF is present which is followed by Li_2CO_3 and finally $(CH_2OCO_2Li)_2$ (Figure 2b). Analysis of the formation process revealed that at first reactions are dominating but later on diffusion is the main driving force. Moreover, the geometric analysis provided a native SEI height of $31\,Å$ with a volume fraction of $40\,\%$. Furthermore, a dyadic volume fraction composition could be observed. These findings enhance the understanding of the SEI structure, which can be used during battery characterization e.g., via understanding the battery's impedance spectra and consequentially the internal SEI resistance.

In conclusion, this novel modelling approach allows an unprecedented in-depth analysis of processes during native SEI formation and their impact on safety/durability and may be used for the analysis of other electrochemical systems, too.

Figure 2: (a) Modeled KMC processes. (b) SEI build-up at lithium electrolyte interphase incl. species distribution.

[1]   C. Fang et al., Trends Chem. **1** (2), 152–158 (2019).