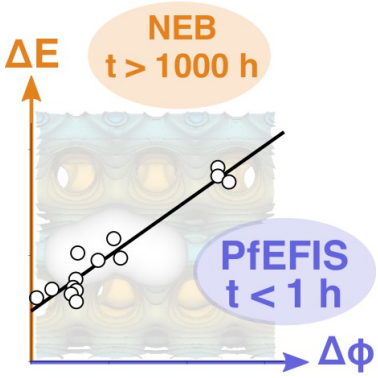
Potential of Electrostatics-Finite Ion Size (PfEFIS) method: towards automatic ion diffusion network analysis in solids

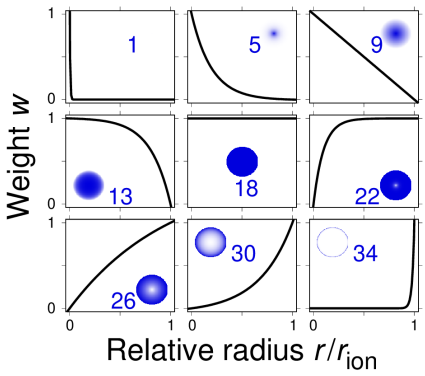
Nils E. R. Zimmermann

Lawrence Berkeley National Laboratory, Berkeley, CA, U. S. A.

We use more and more hand-held electronic devices and laptops, and, on our streets, there is a clear shift from predominantly gasoline-powered mobility towards a sizable share of electric mobility. Consequently, the demand for rechargeable battery materials constantly and swiftly increases. Finding new safe and ecological cathode materials for high-energy-density rechargeable batteries is thus an important present-day and future task for the scientific community at the interface between chemistry, physics, materials science, and engineering. Replacing lithium with magnesium as charge carrier could help addressing safety and environmental issues with current technologies. Because experimental screenings take a lot of time and are expensive, computational materials screenings based on efficient quantum mechanical calculations have become attractive alternatives. The assessment of the ionic mobility (i.e., the ion diffusion) is a bottleneck in this context due to the huge computational resources required by the conventionally employed density functional theory-nudged elastic band (DFT-NEB) calculations. For these reasons, we have developed a method, the potential of electrostatics-finite ion size (PfEFIS) barrier estimation method, which can rapidly estimate jump-diffusion barriers of ions in typical battery candidates [1]. The computational speed-up factor of approximately 10,000 (Figure left) thus permits targeting tens of thousands of materials to be screened for their ionic mobility.

The key idea of PfEFIS is to relax a chain of states in the field of the electrostatic potential that is averaged over a spherical volume using different finite size ion models (Figure right). For magnesium migrating in typical battery material candidates such as transition metal oxides, we find that the optimal model is a shell that is slightly larger than usual ion sizes found in literature [2]. This data-driven result parallels typical assumptions made in models based on Onsager's reaction field theory to quantitatively estimate electrostatic solvent effects. We believe that the method can potentially also be used to estimate proton and oxygen ion migration in solid materials, thus, facilitating computational screening studies for solid oxide fuel cells.





Work is in progress, which addresses another important challenge: automatically identifying insertion sites in the (initially empty) materials. This step would be executed prior to the PfEFIS barrier estimation in a high-throughput computational screening. Hence, reliable site identification is of particular importance in order to fully evaluate the entire diffusion network of ions in battery candidate materials in an automatic way. Preliminary results indicate that PfEFIS is also capable of tackling this issue, thus, paving the way to automatically handling ten thousands of materials in computational work flows for battery materials discovery.

[1] N. E. R. Zimmermann, D. C. Hannah, Z. Rong, M. Liu, G. Ceder, M. Haranczyk, K. A. Persson, *J. Phys. Chem. Lett.* **2018**, 9, 628–634.

[2] R. D. Shannon, *Acta Cryst.* **1976**, A32, 751–767.