Advances in Supercapacitor Modeling with Flexible, Disordered Electrodes

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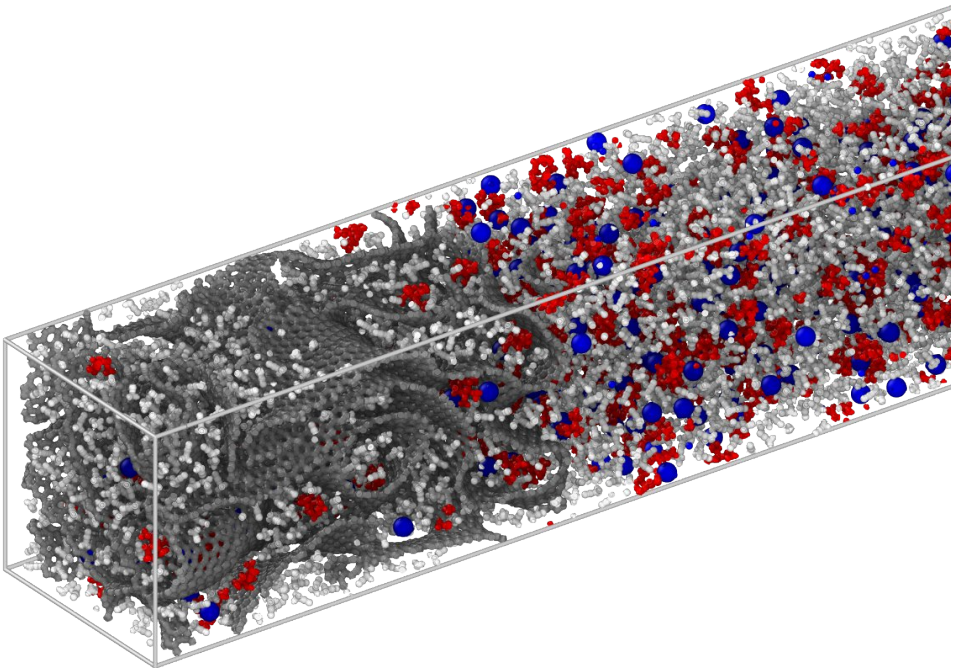
Molecular simulations have become indispensable for characterizing the charging mechanisms of electrical double-layer capacitors. However, a significant gap remains between theoretical models and experimental reality, partly due to the approximation of rigid electrode frameworks and simplified pore geometries. In this work, we overcome these limitations by integrating constant-potential molecular dynamics with advanced machine-learning potentials to investigate the distinct roles of electrode flexibility [1] and structural disorder [2] on supercapacitor performance.

First, by employing a machine-learning potential for carbon to permit atomic relaxation, we compare rigid versus flexible nanoporous sp2/sp3 electrodes in ionic liquid electrolytes. We demonstrate that electrode flexibility significantly enhances in-pore ionic diffusivity, shortening the characteristic charging time by a factor of 3 compared to rigid analogues. This kinetic boost is driven by the electrode's "breathing modes," which mitigate pore overcrowding and accelerate co-ion expulsion without compromising specific capacitance.

Second, we extend this approach to realistic, large-scale systems. Using controlled quench dynamics, we generated disordered nanoporous graphitic structures to systematically study the effect of pore topology. By applying constant potential MD to these realistic architectures, we successfully retrieve the anomalous increase in carbon capacitance at pore sizes below 1 nanometer [3]. Our findings provide a view of how mechanical flexibility regulates charging kinetics while pore size distribution dictates capacitance, offering new guidelines for the design of optimized carbon electrodes.



Snapshot of nanoporous carbon electrodes with TEA/BF4 liquid electrolyte.

[1] Zacharie Waysenson, Arthur France-Lanord, Alessandra Serva, Patrice Simon, Mathieu Salanne, and A. Marco Saitta
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[2] Zacharie Waysenson, Arthur France-Lanord, Alessandra Serva, Patrice Simon, Mathieu Salanne, and A. Marco Saitta
In preparation
[3] J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, and P. L. Taberna
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