Influence of Cu(111) and Ni(111) Substrates on the Capacitances of Monolayer and Bilayer Graphene Supercapacitor Electrodes

The quantum capacitance model based on graphene's fixed-band density of states (DOS) is one of the most popular approaches to modeling the capacitive behavior of graphene-based supercapacitor electrodes. This model, however, consistently over-estimates the capacitance of graphene electrodes by an order of magnitude compared to experimental measurements. Moreover, the influence of conducting substrates used as electrical contacts for graphene is typically excluded altogether by its representation as an infinite capacitance connected in series with the quantum capacitance of pristine graphene. This is despite the significant change in the electrode's total DOS because of graphene's adsorption to the substrate. Using insights from density functional theory calculations, we present a general model for calculating electrode capacitance based on space charge distribution in graphene-metal junctions. The model predicts capacitance values ranging between 1.4 and 1.7 μF cm⁻² for graphene on Cu(111) and Ni(111), which match closely with the experimentally reported range of 2-6 μF cm⁻². The model also predicts a constant capacitance for monolayer and bilayer graphene on Cu(111) and Ni(111), which challenges the popular assumption that the slightly field-tunable capacitance observed in practical supercapacitors can be attributed to the quantum capacitance of graphene in isolation from interactions with substrates and electrolytes.