Deciphering Electrochemical Processes Occurring Under a Graphene Membrane

Sidney R. Cohen[1], Salma Khatun[2], Sa'ar Shor Peled[2], Irit Rosenhek-Goldian[1], Robert S. Weatherup[3], Baran Eren[2]

1. Department of Chemical Research Support, Weizmann Institute of Science, ISRAEL
2. Department of Chemical and Biological Physics, Weizmann Institute of Science, ISRAEL
3. Department of Materials, University of Oxford, United Kingdom

The ability to probe chemical and physical processes occurring in solution at small scales is developing rapidly. Whereas recent advances in 3D SPM provide molecular-structuring information, and scanning ion conductance microscopy can provide electrochemical information at tens of nm resolution, a greater suite of established techniques is available for measurements made in air or vacuum conditions. Therefore, a second approach is to enclose a solution system by a very thin upper membrane which is transparent to radiation and/or electrons, enabling high resolution surface measurements of processes occurring at the interfacial liquid region. Graphene is an excellent choice of such membrane, being very thin yet mechanically robust. This concept has been applied recently in several studies. Nonetheless, interpretation of such measurements must account for graphene doping, width of double layer in liquid, influence of the graphene electromechanical response, and artifacts due to graphene contamination during preparation of the cell. In this work we apply scanning kelvin probe microscopy to study miniature cells with 500 nm diameter capped by graphene. The contact potential difference (CPD) was measured for systems at 2 different pH values (9 and 10, i.e., 10^{-3} and 10^{-4} M NaOH), as a function of voltage applied between the single layer graphene membrane and a Pt counter electrode located remotely in the solution. We found that the changes in CPD can be explained by the electric double layer thickness and changes in the graphene doping due to the gating of the liquid cell. At higher voltages, CPD and topographical changes provided evidence of reversible graphene functionalization and electro-wetting, which will also be discussed. The graphene membrane is robust to scanning and allows direct measurement of phenomena occurring near the lower liquid/graphene interface. The insights gained here provide a sound basis for further studies on more complex systems.