

## Abstract

The complex interplay between the material's properties and the electrochemical process often taking place at its ubiquitous edges makes it difficult to discriminate the role of single defects in the charge transfer processes in the material. Therefore, we have performed *in-situ*  $\mu$ -droplet Raman spectroelectrochemistry (SEC) to identify the localized charge transfer processes through the basal plane and defects in a selected localized area of 10-20  $\mu\text{m}^2$  of defect-free and defective monolayer graphene. It is noticed that two distinctive electron transfer processes of slower and faster rates exist side-by-side in the same sample but they are confined in the defect-free and defect-rich regions, respectively. Furthermore, in order to explore the electrochemical ion intercalation mechanism for rechargeable batteries, *in-situ* Raman SEC in a macro SEC cell was performed. It was observed that structural properties such as the lateral domain size ( $L_a$ ), degree of graphitization ( $g$ ), inter-defect distance ( $L_D$ ) and defect density ( $n_D$ ) have substantial influence on the electrochemical (de)intercalation of anion into natural and kish graphite during charge/discharge process. It was also revealed that ultrasound treatment of natural graphite reduces the  $L_a$  which enhances the reversibility of the anion (de)intercalation in a concentrated aqueous electrolyte solution. The reversibility of anion (de)intercalation into highly oriented pyrolytic graphite during discharge process was also evidenced by *in-situ* Raman SEC using water-in-salt electrolyte.