

## Ion Insertion into Porous Carbon Electrodes Investigated by *in-situ* AFM Measurements

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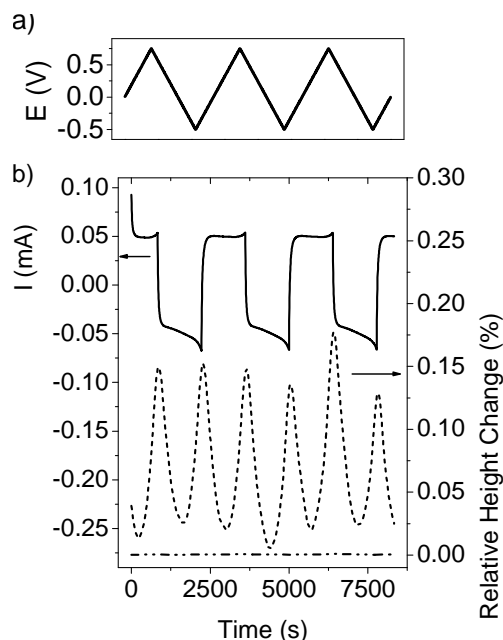
Electrochemical Capacitors (ECs) utilizing porous carbon electrodes store charge in the electrochemical double layer formed at the electrode/electrolyte interface. The lack of Faradaic reactions means no chemical or dimensional changes are expected to occur during charge/discharge. However, electrochemical dilatometry (ED) experiments have shown that porous carbon electrodes actually undergo up to several percent expansion/contraction during charge/discharge.<sup>1,2,3</sup> The volume changes are attributed to ion insertion into the carbon pores, and may have negative effects such as limiting the operating voltage and reducing the lifetime of these devices.<sup>1,2,3</sup>

Recently, *in-situ* Atomic Force Microscopy (AFM) was shown to be a valuable technique to monitor the volume changes experienced during charge/discharge.<sup>4</sup> The advantages of using AFM over macroscopic ED techniques include a high spatial resolution (allows for inspection of individual elements such as grains or particles) and a better resolution in the z-direction (<1 nm for AFM compared to ca. 60 nm for ED).<sup>4</sup>

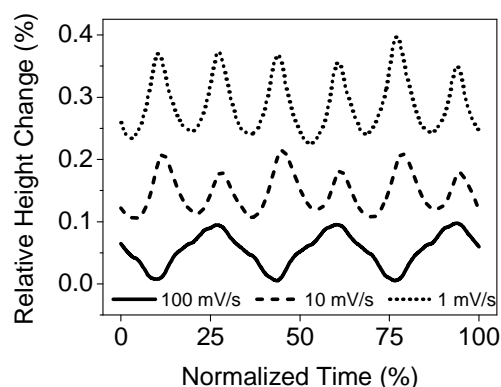
The expansion/contraction of several porous carbon materials in combination with various electrolytes were examined during charge/discharge by means of *in-situ* AFM measurements. All experiments were performed using an *in-situ* electrochemical AFM cell from Asylum Research (USA) and an MFP-3D AFM (Asylum Research, USA) was used to conduct surface displacement measurements. Electrochemical measurements were made using a Bio-Logic SP-200 potentiostat/galvanostat (Bio-Logic, USA).

Cyclic voltammograms are performed on porous carbon working electrodes while both the current response and z displacement data are collected. Figure 1 shows the results of a typical set of data. Figure 1a displays the potential waveform applied to the electrode and Figure 1b shows the current (solid line) and relative height change (dashed line) of a porous carbon electrode. For comparison, Figure 1b also shows the relative height change of a non-porous glassy carbon electrode. No change in height is observed for the non-porous carbon, while the porous carbon clearly experiences changes in volume during charge/discharge which is attributed to anion/cation insertion into the carbon pores. In order to obtain kinetic information regarding the anion/cation insertion, the cyclic voltammetry experiments are performed at various sweep rates allowing for an analysis of the strain profiles as a function of potential sweep rate. Figure 2 shows the strain profiles collected for a porous carbon electrode demonstrating the dependence of the strain profile on potential sweep rate. Here, we will discuss possible strain mechanism and the

influence of pore and ion size on the ion insertion kinetics. The goal is to understand the fundamental processes determining the macroscopic properties and limiting rate capability in order to improve and engineer future ECs.



**Figure 1:** a) Applied potential b) Current response (—) and relative height change of mesoporous carbon electrode (- -) and glassy carbon electrode (- - -).



**Figure 2:** Relative height change of a mesoporous carbon electrode during three consecutive CV cycles performed at various potential sweep rates.

### References

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