Fabrication and Characterization of a Vertically-Oriented Graphene Supercapacitor

National Aeronautics and Space Administration

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Introduction

Supercapacitors, otherwise known as electrical double layer capacitors, are a new type of electrochemical capacitor whose storage capacity is governed by two principals: the electrostatic storage achieved by a separation of charge at the interface of an electrode with an electrolytic solution, and pseudocapacitance, whose electrical energy is achieved by faradaic redox reactions. This project reports the synthesis and characterization of vertically-oriented graphene grown on copper substrates as electrodes in electric double-layer capacitor. Graphene is a two-dimensional pure-carbon material with a high potential for energy storage. With vertically-grown graphene, an exponentially-larger surface area is made available, allowing an increase in electrostatic storage. Nano-sheets of carbon were fabricated via plasma-enhanced chemical vapor deposition and characterized using cyclic voltammetry and Raman spectrometry. Specific capacitance was compared using with both aqueous and organic electrolytes, as well as variations with growth conditions and scan rates. Applications of the supercapacitor range from energy storage in space exploration to consumer electronics and transportation.

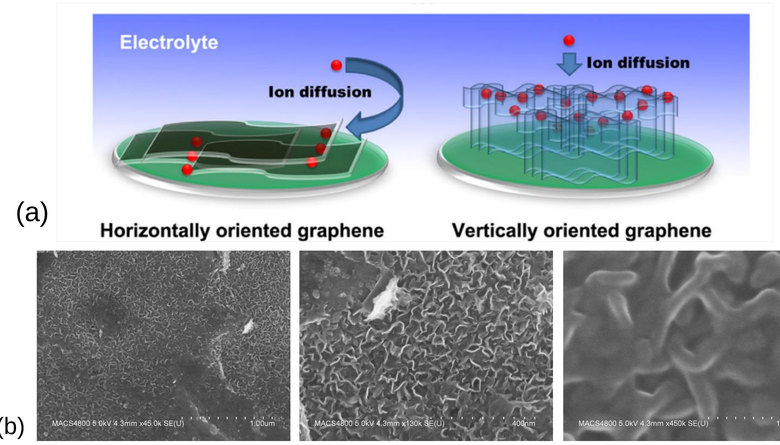

Figure 1. (a) paths of ion diffusion for graphene grown horizontally and vertically. (b) Scanning electron microscope of vertically grown graphene.

Methods

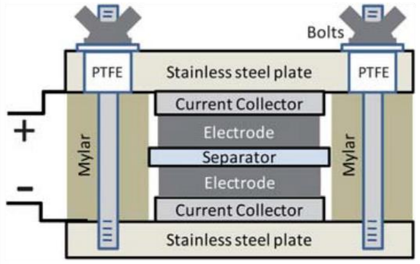

Figure 2. Schematic and setup of the electric double layer capacitor

An electric double layer capacitor was constructed by taking two sheets of copper with grown graphene and sandwiching them with a membrane. The capacitor was then connected to a potentiostat, measuring current vs. voltage. From the slopes produced, capacitance of the capacitor and specific capacitance of the vertically-grown graphene could be found.

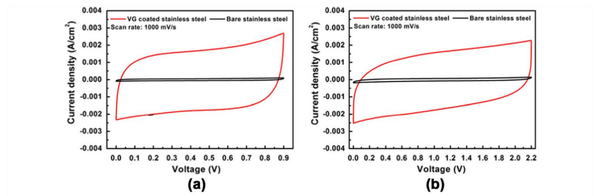

Fig. 3 – Comparison of CV curves of VG-coated stainless steel and bare stainless steel at a scan rate of 1000 mV/s in (a) 6 M

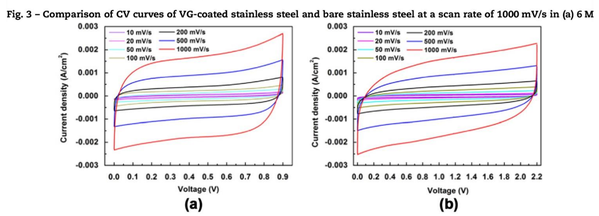

Fig. 4 – CV curves of VG-coated stainless steel at different scan rates in (a) 6 M KOH and (b) 1 M $TEABF_4$/AN.

Figures 3-4 illustrate results of vertically grown graphene on stainless steel substrates. The show that an ideal cyclic voltammetry measurement of a capacitor will show the behavior

$$Q = CV$$

Where Q is the charge and C is the capacitance. Changing the voltage over time the equation becomes

$$\frac{dQ}{dt} = \frac{CdV}{dt}$$

Where $\frac{dQ}{dt}$ is the current and $\frac{dV}{dt}$ is the scan rate. By rearranging, capacitance is calculated as

$$C = \frac{\frac{dQ}{dt}}{\frac{dV}{dt}} = \frac{I}{s}$$

Where I is the current and s is the scan rate.

Results and Discussion

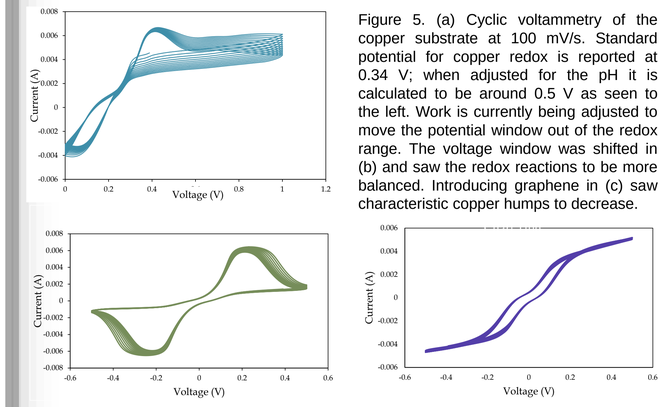

Figure 5. (a) Cyclic voltammetry of the copper substrate at 100 mV/s. Standard potential for copper redox is reported at 0.34 V; when adjusted for the pH it is calculated to be around 0.5 V as seen to the left. Work is currently being adjusted to move the potential window out of the redox range. The voltage window was shifted in (b) and saw the redox reactions to be more balanced. Introducing graphene in (c) saw characteristic copper humps to decrease.

SEM images show that vertical graphene was successfully grown. Cyclic voltammetric measurements with an aqueous electrolyte were dominated by an irreversible redox event occurring with copper. The group identified that measurements need to take place in a different voltage window to avoid these reactions. But the reactions indicate that copper may not be an ideal substrate in these conditions. Data of the capacitor in an organic electrolyte is not yet available. Future research of vertical graphene grown on other materials has been proposed.

Acknowledgments

Shuhei T., Lars D., and Josh P

Bibliography

Illustrations and graphs are from:
Bo, Z.; Wen, Z.; Kim, H.; Lu, G.; Yu, K.; Chen, J. “One-step fabrication and capacitive behavior of electrochemical double layer capacitor electrodes using vertically-oriented graphene directly grown on metal.” *Science Direct. J. Carbon.* **2012**. doi: 10.1016

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