Bipolar Electrochem Graphene Microsupercaps

Iman Khakpour[1], Anis Allagui[1], Xian Pan[2], Yunhe Zhao[2], Chunlei Wang[1,2]*
[1]Department of Mechanical and Materials Engineering, Florida International University
[2]Department of Mechanical and Aerospace Engineering, University of Miami
Corresponding author: wangc@miami.edu

Abstract

This study introduces a successful modification of the bipolar electrochemistry (BPE) method to efficiently produce and deposit high-quality reduced graphene oxide onto a conductive substrate. This innovative approach integrates material production and device fabrication into a single-step process that is straightforward, controllable, cost-efficient, and environmentally friendly. Microstructural analysis of the deposited material reveals the formation of oriented graphene sheets on the substrate. For micro-supercapacitor fabrication, interdigitated gold microelectrode arrays are generated through regular photolithography and subsequently employed as the conductive substrate in the BPE process. The electrochemical assessment of the fabricated device through cyclic voltammetry and galvanostatic charge/discharge verifies its outstanding specific areal capacitance. Notably, electrochemical impedance spectroscopy unveils exceptional high-frequency responses, promising potential applications in AC/DC filter systems. A comprehensive presentation of the detailed results will be delivered at the upcoming conference.

Keywords: Bipolar electrochemistry, Exfoliation, Graphene, Micro-supercapacitors, AC/DC filter

Introduction

Bipolar electrochemistry (BPE) refers to the phenomenon in which asymmetric polarization and redox reactions are wirelessly induced on a bipolar electrode (BE) under a sufficient electric field existing between two conductive feeding electrodes. Consequently, due to the spatial variation of the BE/solution potential, reduction and oxidation reactions occur simultaneously at both extremities of the BE [1-3]. BPE has found numerous intriguing applications across various scientific and engineering disciplines, such as micro and nanofabrication[4,5], propulsion of small objects in a solution[6], as well as in electroanalytical and sensing devices [7,8]. Recently, BPE has been demonstrated as a promising 3-in-1 manufacturing approach for exfoliation, reduction, and deposition of 2D Van der Waals materials, such as graphene and phosphorene, in DI water [1, 9-13]. In our work, we improved the BPE method and successfully deposited high-quality reduced graphene oxide (rGO) on the negative feedback electrode through this improved method [9]. We decoupled the cathodic and anodic exfoliation to understand the BPE mechanism [12]. Furthermore, we developed a process to integrate graphene on microelectrodes, and demonstrated good capacitive performance for AC/DC filtering application [13].

BPE and Microelectrodes

By dividing BE into two parts and modifying the typical BPE cell, as shown in Fig. 1(a), we were able to monitor changes in bipolar current and total current passing through the two feeding electrodes. The increase of bipolar current during the BPE process is an indicator of the acceleration of the exfoliation process [9]. By using the modified BPE cell, we have demonstrated that high quality rGO can be formed on negative feeding electrode and graphene oxide (GO) can be formed on positive feeding electrode. BPE has been proved to be a promising environmentally friendly method for the exfoliation, reduction, and deposition of graphene. Khakpour et al, further integrated BPE with photolithography process in order to achieve in-situ exfoliation and deposition of high quality rGO on microelectrodes [14]. As shown in Fig. 1(b), gold-based interdigitated micro-current collectors (Au-MCC) were fabricated using photolithography method. To avoid the lateral deposition of rGO in between the microelectrodes, a sacrificial photoresist layer was patterned between the interdigitated gold microelectrodes. Fig. 1(c) shows a schematic drawing of the modified BPE cell in DI water employed for deposition of vertically aligned rGO on the Au-MCC, which is mounted on a piece of stainless steel as a negative feeding electrode. After deposition of rGO on the Au-MCC, the sacrificial photoresist patterns were removed and a high fidelity rGO-based microsupercapacitor (rGO-MSC) was formed.

Energy Harvesting and Storage: Materials, Devices, and Applications XIV, edited by
Peter Bermel, Naresh C. Das, Zunaid Omair, Proc. of SPIE Vol. 13027, 1302704

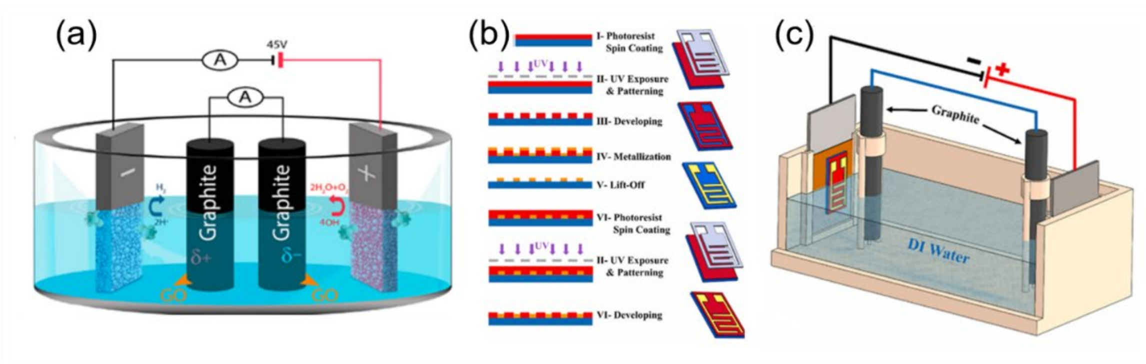

Figure 1. (a) Schematic of the new bipolar electrochemical setup [9]. (b) Illustration of the fabrication process of the interdigitated Au-MCC. (c) Schematic drawing of the BPE setup for fabricating the rGO-MSC [14]

Performance and Application

Our results demonstrated that highly reduced graphene layers with porous structure could be formed on the negative electrode using modified BPE cell. As shown in Fig. 2(a) and 2(b), detailed cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) were conducted to verify the electrochemical performance of the rGO-based electrodes. The electrochemical characterization revealed that the rGO-based thin film electrode on stainless steel substrate has a high areal capacitance of 2 mF cm^{-2} at the scan rate of 2 mV s^{-1} [9]. The rGO-MSC could deliver a specific capacitance of ~640 μF cm^{-2} at a scan rate of 2 mV s^{-1} [14]. As shown in Fig. 2 (c) and 2 (d), from electrochemical impedance spectroscopy (EIS) study, it was also found that close to ideal capacitive behavior at frequencies lower than 1000 Hz. The phase angle and specific capacitance of the rGO-MSC measured at 120 Hz were −81.2 deg and 65.2 μF cm^{-2} [14], which indicate its promising application in AC/DC filtering. Furthermore, the cut-off frequency (i.e., phase angle is -45 deg) of 3974 Hz for the freshly prepared MSC and 3486 Hz after 50000 consecutive charge/discharge cycles indicate excellent stability of the rGO-MSC. Finally, the rGO-MSC device has been validated in an actual AC filtering circuit, compared to using a traditional aluminum electrolytic capacitor, excellent AC/DC filtering performance was observed.

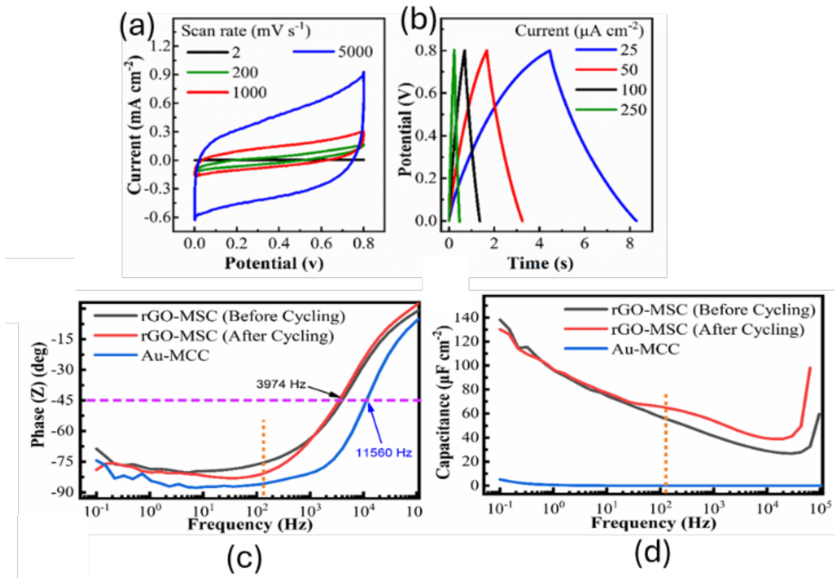

Figure 2. (a) Cyclic voltammetry at different scan rates, and (b) galvanostatic charge-discharge results at different current densities, of the fabricated rGO-MSC. (c) The impedance phase angle as a function of frequency (bode phase plot), and (d) specific areal capacitance as a function of frequency, for Au-MCC and rGO-MSC before and after 50000 cycling [14].

Conclusions

We have demonstrated an eco-friendly approach for exfoliation, reduction and deposition of graphene using modified BPE approach. The vertically aligned and highly rGO nanosheets were deposited on the Au-MCC to form rGO-MSC. Time-domain and frequency-domain electrochemical analysis of the rGO-MSC device demonstrates excellent stability and high electrochemical performance at high frequencies. Replacing a traditional aluminum electrolytic capacitor using the rGO-MSC in standard AC filtering circuit demonstrated the promising application of rGO-MSC in AC/DC filtering.

Acknowledgement

The authors gratefully acknowledge the support of the National Science Foundation (NSF) under award # 2423124.

References

[1] A. Allagui, M. A. Abdelkareem, H. Alawadhi, and A. S. Elwakil, "Reduced Graphene Oxide Thin Film on Conductive Substrates by Bipolar Electrochemistry," Sci Rep, vol. 6, no. 1, p. 21282, Feb. 2016, doi: 10.1038/srep21282.

[2] S. E. Fosdick, K. N. Knust, K. Scida, and R. M. Crooks, "Bipolar Electrochemistry," Angew Chem Int Ed, vol. 52, no. 40, pp. 10438–10456, Sep. 2013, doi: 10.1002/anie.201300947.

[3] L. Koefoed, S. U. Pedersen, and K. Daasbjerg, "Bipolar electrochemistry—A wireless approach for electrode reactions," Current Opinion in Electrochemistry, vol. 2, no. 1, pp. 13–17, Apr. 2017, doi: 10.1016/j.coelec.2017.02.001.

[4] J.-C. Bradley et al., "Creating electrical contacts between metal particles using directed electrochemical growth," Nature, vol. 389, no. 6648, pp. 268–271, Sep. 1997, doi: 10.1038/38464.

[5] C. Warakulwit et al., "Dissymmetric Carbon Nanotubes by Bipolar Electrochemistry," Nano Lett., vol. 8, no. 2, pp. 500–504, Feb. 2008, doi: 10.1021/nl072652s.

[6] G. Loget and A. Kuhn, "Electric field-induced chemical locomotion of conducting objects," Nat Commun, vol. 2, no. 1, p. 535, Nov. 2011, doi: 10.1038/ncomms1550.

[7] S. Munktell, M. Tydén, J. Högström, L. Nyholm, and F. Björefors, "Bipolar electrochemistry for high-throughput corrosion screening," Electrochemistry Communications, vol. 34, pp. 274–277, Sep. 2013, doi: 10.1016/j.elecom.2013.07.011.

[8] S. E. Fosdick and R. M. Crooks, "Bipolar Electrodes for Rapid Screening of Electrocatalysts," J. Am. Chem. Soc., vol. 134, no. 2, pp. 863–866, Jan. 2012, doi: 10.1021/ja210354m.

[9] I. Khakpour, A. Rabiei Baboukani, A. Allagui, and C. Wang, "Bipolar Exfoliation and in Situ Deposition of High-Quality Graphene for Supercapacitor Application," ACS Appl. Energy Mater., vol. 2, no. 7, pp. 4813–4820, Jul. 2019, doi: 10.1021/acsaem.9b00479.

[10] A. Allagui, J. M. Ashraf, M. Khalil, M. A. Abdelkareem, A. S. Elwakil, and H. Alawadhi, "All‐Solid‐State Double‐Layer Capacitors Using Binderless Reduced Graphene Oxide Thin Films Prepared by Bipolar Electrochemistry," ChemElectroChem, vol. 4, no. 8, pp. 2084–2090, Aug. 2017, doi: 10.1002/celc.201700266.

[11] H. Hashimoto, Y. Muramatsu, Y. Nishina, and H. Asoh, "Bipolar anodic electrochemical exfoliation of graphite powders," Electrochemistry Communications, vol. 104, p. 106475, Jul. 2019, doi: 10.1016/j.elecom.2019.06.001.

[12] I. Khakpour, A. Rabiei Baboukani, A. Allagui, A. Hachicha, C. Wang, On the Mechanistic Pathways of Exfoliation-and-Deposition of Graphene by Bipolar Electrochemistry, Nanotechnology, May 2021, https://doi.org/10.1088/1361-6528/ac037c.

[13] A. Rabiei Baboukani, I. Khakpour, V. Drozd, A. Allagui, and C. Wang, "Single-step exfoliation of black phosphorus and deposition of phosphorene via bipolar electrochemistry for capacitive energy storage application," J. Mater. Chem. A, vol. 7, no. 44, pp. 25548–25556, 2019, doi: 10.1039/C9TA09641H.

[14] I. Khakpour, A. R. Baboukani, S. Forouzanfar, A. Allagui, and C. Wang, "In-situ exfoliation and integration of vertically aligned graphene for high-frequency response on-chip microsupercapacitors," Journal of Power Sources, vol. 516, p. 230701, Dec. 2021, doi: 10.1016/j.jpowsour.2021.230701.