



Experimental and modeling study on charge storage/transfer mechanism of graphene-based supercapacitors



Shuai Ban ^a, Xie Jing ^a, Hongjun Zhou ^a, Lei Zhang ^{b,*}, Jiujuan Zhang ^b

^a Institute of New Energy, University of Petroleum, 18 Fuxue Road, Changping, Beijing 102249, China

^b Energy, Mining & Environment Portfolio, National Research Council of Canada, Vancouver, BC V6T 1W5, Canada

HIGHLIGHTS

- A graphene-based supercapacitor is studied using a multidisciplinary approach.
- Capacitance of graphene is limited by internal resistance and mass transfer.
- Molecular simulation shows hindered ion diffusion in 2D confinement of graphene.
- Graphene can adaptively optimize its porous structure during charging process.

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ABSTRACT

A symmetrical graphene-based supercapacitor is constructed for studying the charge-transfer mechanism within the graphene-based electrodes using both experiment measurements and molecular simulation. The in-house synthesized graphene is characterized by XRD, SEM and BET measurements for morphology and surface area. It is observed that the electric capacity of graphene electrode can be reduced by both high internal resistance and limited mass transfer. Computer modeling is conducted at the molecular level to characterize the diffusion behavior of electrolyte ions to the interior of electrode with emphasis on the unique 2D confinement imposed by graphene layers. Although graphene powder poses a moderate internal surface of $400 \text{ m}^2 \text{ g}^{-1}$, the capacitance performance of graphene electrode can be as good as that of commercial activated carbon which has an overwhelming surface area of $1700 \text{ m}^2 \text{ g}^{-1}$. An explanation to this abnormal correlation is that graphene material has an intrinsic capability of adaptively reorganizing its microporous structure in response to intercalation of ions and immergence of electrolyte solvent. The accessible surface of graphene is believed to be dramatically enlarged for ion adsorption during the charging process of capacitor.

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1. Introduction

In recent years, electrochemical supercapacitors have being recognized as the feasible energy storage and conversion devices for transportation, stationary and portable power applications. In terms of technology commercialization, supercapacitors have been becoming the competitive options for specific applications, including electric hybrid vehicles, digital communication devices, digital cameras, electrical tools, pulse laser technique, uninterruptible power supplies, and energy storage devices for solar

cells [1,2]. The great R&D interesting in supercapacitor technique can be attributed to their advantages include high power density, long cycle-life, high efficiency, wide range of operating temperature, environmental friendliness, and safety, as well as its function of bridging gap between high power density of traditional dielectric capacitors and high energy density of batteries/fuel cells [3]. However, one of the major challenges that strongly impedes a worldwide spread of supercapacitors is their low energy density [4]. To overcome this challenge, the major R&D effort has been put onto both strategic material selection and innovative system design [5]. Particularly, development of novel materials, including both electrode and electrolyte materials, is expected to have opportunity for achieving technology breakthroughs in near future.

As one type of new carbon materials, graphene has attracted great attention in both academia and industry worldwide in the most recent years [6,7]. Graphene is a 2D single layer of sp²-bonded

* Corresponding author. 4250 Wesbrook Mall, Building VAN-2, Room 2230, Vancouver, BC V6T 1W5, Canada. Tel.: +1 604 221 3000x5504; fax: +1 604 221 3001.

E-mail address: lei.zhang@nrc.gc.ca (L. Zhang).

carbon, which is considered as the basic construction unit for carbon materials with various forms [8]. Due to its unique morphology, graphene can offer a series of prominent intrinsic chemical and physical features, as well as excellent mechanical and electrical properties [9,10]. Attracted by these unique properties, many researchers have explored graphene-based materials as the supercapacitor electrode materials in the effort to increase the energy density [11–13]. However, although graphene samples prepared using various synthesis approaches have been demonstrated to be the promising materials for supercapacitors with relatively high energy density [5,14–16], the charge storage mechanism associated with this unique carbon material is still unclear.

In this work, a series of electrochemical measurements including cyclic voltammograms, galvanic charging/discharging cycles and electrical impedance were conducted, and the difference of electrochemical performance between graphene and activated carbon was compared in relation to their distinct micro-structures. Furthermore, computer simulation was also performed at the molecular level to investigate mass transfer of electrolyte ions in graphene-based electrode. The proposed charging mechanism of graphene-based supercapacitors was also concluded to provide future materials design researches with a solid theoretical guidance.

2. Experimental

2.1. Synthesis of graphene

The graphene material was prepared by using microwave exfoliation of graphite oxide (GO) through two major steps [17]. At first, the pristine graphite flake (GF) was oxidized to graphite oxide using a modified Hummer's method [18]. In detail, a mixture of 10 g GF (Alfa Aesar, median 7–10 micro, 99% metal basis) and 7.5 g NaNO_3 (Aldrich) was dispersed in 345 ml 98% sulfuric acid (Aldrich) in ice bath. Then, 45 g KMnO_4 (Aldrich) was slowly added into the slurry with mild stirring. After that, the reaction mixture was kept at 35 °C and stirred for 4 days. To terminate the oxidation reaction, 500 ml water was slowly added, followed by dripping 30% H_2O_2 until bubbling stops. The slurry was poured into another 1.5 L water and stored for 12 h to obtain the brownish yellow precipitate. The precipitate was washed using DI water and centrifuged at 10,000 rpm several times until its pH reaches neutral. Finally, GO was collected after drying overnight at 60 °C. In the second stage, GO exfoliation was achieved in aid of microwave irradiation. Typically, 1 g of GO was vacuumed and sealed in a flask under N_2 atmosphere. The flask was then transferred to microwave oven and treated at a power of 1200 W. The violent exfoliation of GO occurs under microwave irradiation after a few seconds. The obtained fluffy graphene powder (MRGO) was further washed and filtrated to remove SO_4^{2-} , and stored at 80 °C for a later use.

2.2. Characterization of graphene

Microstructure and morphology of graphene were characterized using XRD (Bruker D8 diffractometer with $\text{Cu K}\alpha$ radiation in a range of diffraction angle from 5° to 35°), SEM (Hitachi S-3500N scanning electron microscope with an operating voltage of 20 kV), and nitrogen sorption analysis (Beckman Coulter SA 3100 surface area and pore size analyzer).

2.3. Electrochemical measurements

The ink of fluffy graphene powder (MRGO) was prepared by mixing 5 wt% polytetrafluoroethylene (PTFE, Aldrich) binder 95 wt

% carbon mixture containing MRGO and conductive carbon Super P[®] Li (TIMCAL) and isopropanol at a concentration of 4 mg ml^{-1} . Typically, 20 ml MRGO ink was treated using a sonication probe at a power of 175 W for 1 h, followed by deposition on two $2 \times 2 \text{ cm}^2$ Ni current collectors via drop-coating. For comparison, the commercially available activated carbon RP20 (from Kuraray Chemical Co.) specially design for electric double-layer capacitors were used through the similar electrode preparation procedure. These two electrodes were sandwiched with a 30 μm thick porous PTFE separator (W.L. Gore & Associates, Inc.) in between, forming an electrode separator assembly (ESA). This ESA was then assembled into a two-electrode test cell, followed by impregnation in aqueous electrolyte of 0.5 M Na_2SO_4 in a vacuum oven at 60 °C for at least 1 h [19]. For electrochemical measurements, cyclic voltammograms and galvanic charging–discharging curves were recorded using a Solartron 1287 potentiostat. For cell internal resistance measurement, a Tsuruga 3566 AC m-ohm Tester was operated in an AC frequency range from 0.01 Hz to 1 kHz. All measurements were conducted at room temperature and ambient pressure.

2.4. Molecular simulation

A simplified 2D model of graphene array was developed to investigate mass transport phenomenon in supercapacitor electrodes. Graphene was generally represented by a stack of straight carbon walls. The atomic interval of carbon was chosen to be 0.34 nm, while the interlayer distance of graphene layers was selected to be 1.02 nm. Either 1 or 2 holes with a width of 1.02 nm were created on each carbon wall, resembling diffusion path through vacancy defects on the individual graphene surface or gaps between adjacent graphene edges. In total, 10 carbon walls were fixed in parallel along Y axis, and each wall consisted of 30 carbon atoms. Two moving particles were initially placed in each channel between neighboring carbon walls. The dimension of simulation box was $10.2 \times 10.2 \text{ nm}^2$, and periodic condition was applied to all directions. For the sake of convenience, all particles used the 12-6 Lennard–Jones parameters of sp²-bonded carbon taken from gro-macs force field [20,21], i.e. $\epsilon = 0.0024135 \text{ eV}$, $\sigma = 0.34 \text{ nm}$. Molecular dynamics modeling in NVT ensemble was performed using Lammmps [22]. Time step was chosen to be 2 fs, and temperature was 300 K, which was only coupled to moving particles. The NVT simulation was running for 10^7 steps. Mean squared displacement (MSD) was calculated as a function of time, while diffusion coefficients were calculated by linear regression of MSD curves in the range of 0– 10^4 ps.

3. Results and discussion

3.1. Material characterization

Structural characterization measurements are often used to identify the dispersion of graphene sheets from graphite precursors [23,24]. Starting from graphite flakes, graphene powder was obtained from microwave assisted reduction of graphite oxide. XRD patterns of typical products involved in this synthesis path are shown in Fig. 1(a). It can be seen that the pristine graphite poses one diffraction peak located at about 27°, corresponding to an interlayer distance of 0.33 nm. Upon strong oxidization, graphene layers are effectively separated to an average distance of 0.8 nm due to most occupancy of oxygen-based functional groups on graphene surface. During reduction process, exfoliation of graphene layers rapidly takes place due to the large internal stress induced by gas release from graphite oxide. Graphene crumple and stacking can be observed from SEM image in Fig. 1(b). Such an irregularly folding structure leads to the disappearance of XRD peaks as seen in

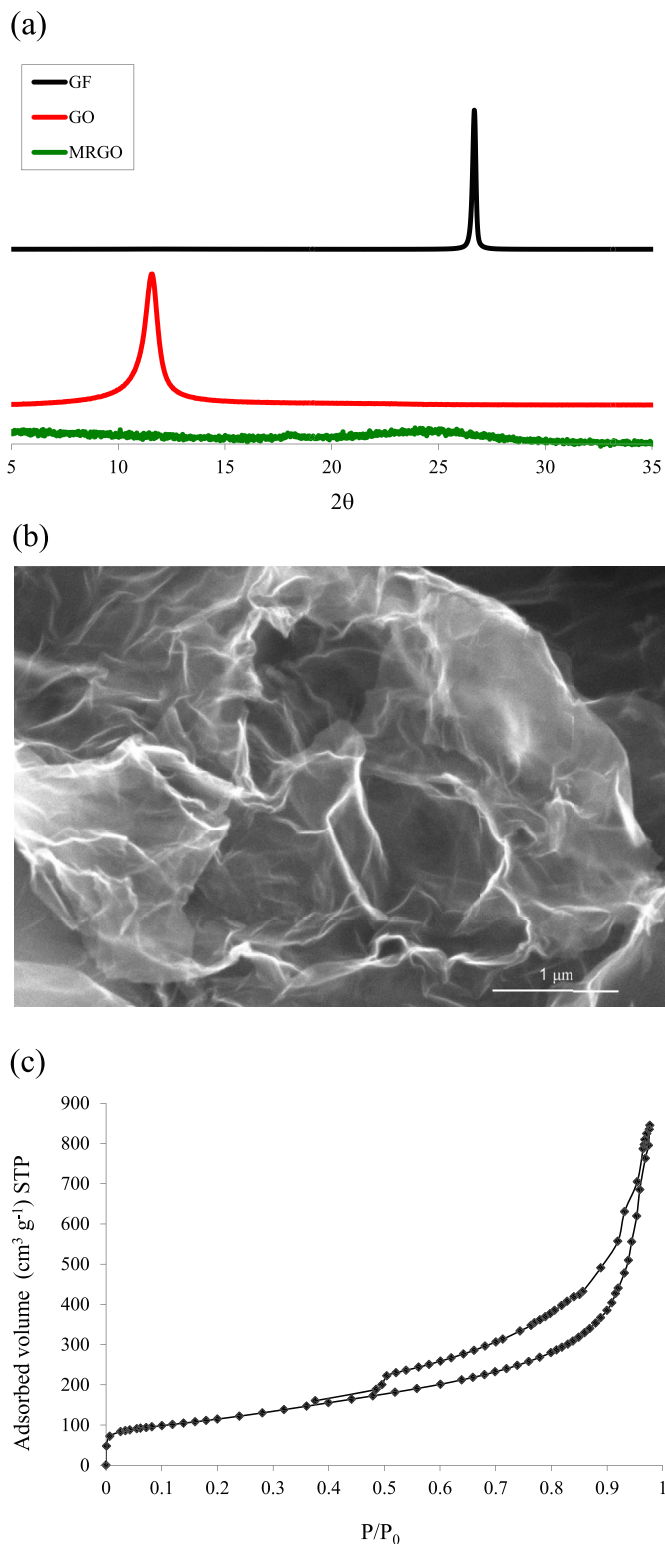


Fig. 1. Structural characterization of microwave reduced graphene powder using (a) XRD, (b) SEM, and (c) N_2 physisorption analysis.

Fig. 1(a). Micropore formation in graphene aggregates is quantitatively conformed by BET data plotted in **Fig. 1(c)**, showing a reasonable surface area of $400 \text{ m}^2 \text{ g}^{-1}$ and a total pore volume of $1.5 \text{ cm}^3 \text{ g}^{-1}$. It is noted that porosity of graphene powder is generally not as predominant as activated carbon that can easily

reach an overwhelming surface area over $3000 \text{ m}^2 \text{ g}^{-1}$ [25]. Because the large internal surface and optimal pore size distribution are crucial to charge storage [26], a convincing explanation of graphene's capacitance performance in term of its moderate porous framework is needed for a mechanistic understanding.

3.2. Effect of mass transfer

Fig. 2 shows the cyclic voltammograms and discharging curves of a symmetrical supercapacitor cell with graphene electrodes with different thickness. From **Fig. 2(a)**, it can be seen that the calculated capacitance decreases consistently with increasing both potential scan rate and thickness of electrode layer. The negative effect of electrode thickness originates mainly from the high internal resistance of graphene, which can be qualitatively evidenced from voltage drops of discharging curves at the time $t = 0$ shown in **Fig. 2(b)**. To confirm this, Impedance measurements were also carried out, and the obtained results further supported this assessment by quantifying capacitor's resistance of 0.2Ω for electrode thickness of $15 \mu\text{m}$, 0.26Ω for $30 \mu\text{m}$, and 0.63Ω for $70 \mu\text{m}$, respectively. On the other hand, poor mass transport inside graphene is clearly reflected from the decay of electric capacity with

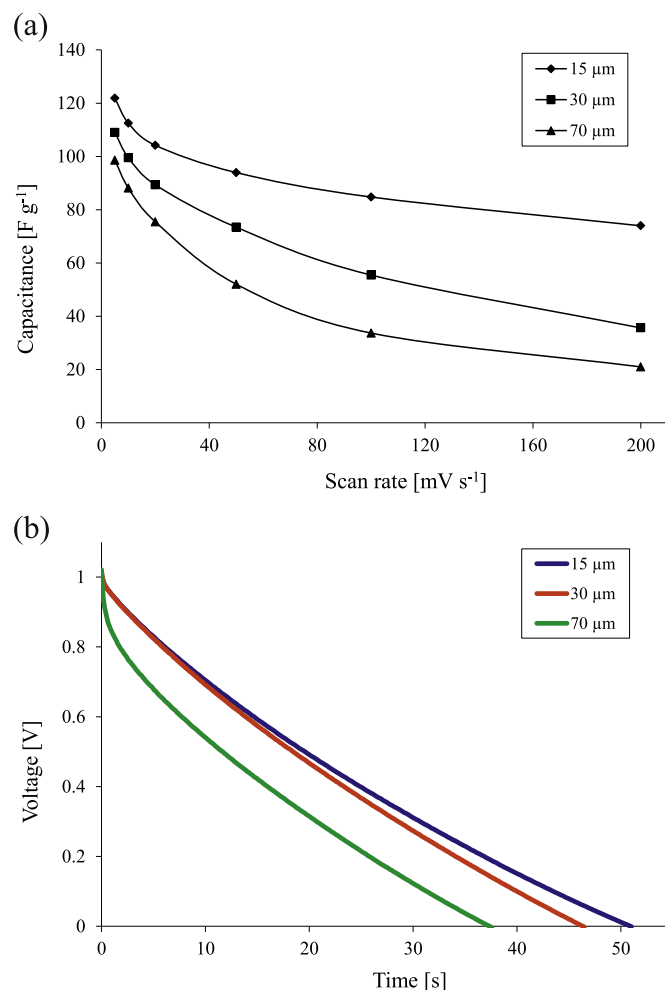


Fig. 2. (a) Capacitance and (b) galvanic discharging of supercapacitor with graphene electrodes with different thickness. The cell capacity is calculated by integrating cyclic voltammograms in the range of 0–1 V. The discharging current is controlled steadily at 1 A g^{-1} . Loadings of graphene with 5 wt% PTFE binder on current collectors are 1 mg cm^{-2} , 2 mg cm^{-2} , and 4 mg cm^{-2} , resulting in electrode thickness of $15 \mu\text{m}$, $30 \mu\text{m}$, and $70 \mu\text{m}$, respectively.

scan rate as shown in Fig. 2(b). In particular, the capacity of electrode with a thickness of $70\text{ }\mu\text{m}$ decreases from 100 F g^{-1} at a scan rate of 5 mV s^{-1} to merely 21 F g^{-1} at 200 mV s^{-1} . Such a dramatic change indicates that even though structural opening of graphite was achieved in the oxidation–reduction process, electrolyte ions still experience difficulty of penetrating into crumpled graphene aggregates. Moreover, it is noted that the as-prepared graphene electrode may possess lower electrochemical capacitance and charge–discharge performance than some of activated carbon [1]. The experimental measurements still reflect typical electrochemical properties of graphene materials, which exceed the capacitance of porous carbon with equivalent surface areas.

For understanding this observation, molecular simulation was employed to assist the investigation of mass transfer phenomenon in graphene. Graphene electrode coated on current collectors was simplified as a 2D array of defective carbon walls fixed in parallel in the simulation box. Modeling snapshots shown in Fig. 3 illustrate that due to the 2D confinement of graphene sheets, particle hopping to adjacent channels rarely takes place, while collision to carbon

walls can frequently occur. As expected, this transport limit is less pronounced in the simulation system with more holes on carbon walls. Either vacancy defects or interlayer gaps can bring about available paths for ions transfer. A quantitative analysis of such a dimensional mass transport is performed by calculating particle's diffusivities as seen in Fig. 4. Due to the uniform orientation of carbon layers, particle diffusion is generally faster in X axis than in Y direction by up to one order of magnitude. In particular, self diffusion coefficients in both directions are $D_x = 5.1 \times 10^{-4}\text{ cm}^2\text{ s}^{-1}$, $D_y = 0.5 \times 10^{-4}\text{ cm}^2\text{ s}^{-1}$ for system with 1 hole on each carbon wall, and $D_x = 4.2 \times 10^{-4}\text{ cm}^2\text{ s}^{-1}$, $D_y = 1.3 \times 10^{-4}\text{ cm}^2\text{ s}^{-1}$ for system with 2 holes. When the number of paths across carbon walls doubles, the ratio of diffusivity D_x along channels to diffusivity D_y crossing channels decreases from 10 to 3, indicating charge transfer to the interior of graphene electrode is largely improved. In accordance, it was proposed that diffusion barrier of ions through graphene layers could be overcome by using a capacitor with both electrodes aligned in-plane instead of a face to face configuration [27]. Moreover, we anticipate that the structural reorganization of graphene aggregates may take place when contacting with electrolytes, or during charging and discharging processes. Future researches are encouraged to study the evolution of graphene's microporous structure under typical working conditions of supercapacitor.

3.3. Effect of internal resistance

As discussed above, the relatively poor conductivity of graphene can be attributed to the low capacity of electrodes with large thickness or at high scan rate. As a solution, conductive agent can be added to graphene ink in order to reduce the internal resistance of resulting electrodes. In Fig. 5, the commercially available conductive agent Super P was mixed with graphene at different fractions. Compared to capacitor using pure graphene in Fig. 2(a), even a portion of Super P as low as 5 wt% is capable of doubling the electric capacity from 36 F g^{-1} to 65 F g^{-1} at a high scan rate of 200 mV s^{-1} as shown in Fig. 5(a). However, further increase of Super P's loading leads to a performance loss as this nonporous carbon can only enhance electrode conductivity, but without contributing to charge storage. The effect of conductive agent was quantitatively analyzed in impedance measurement in Fig. 5(b). When mixing graphene with only 5 wt% Super P, the internal resistance of capacitor is effectively reduced from $0.26\text{ }\Omega$ to $0.11\text{ }\Omega$. In general, the limited

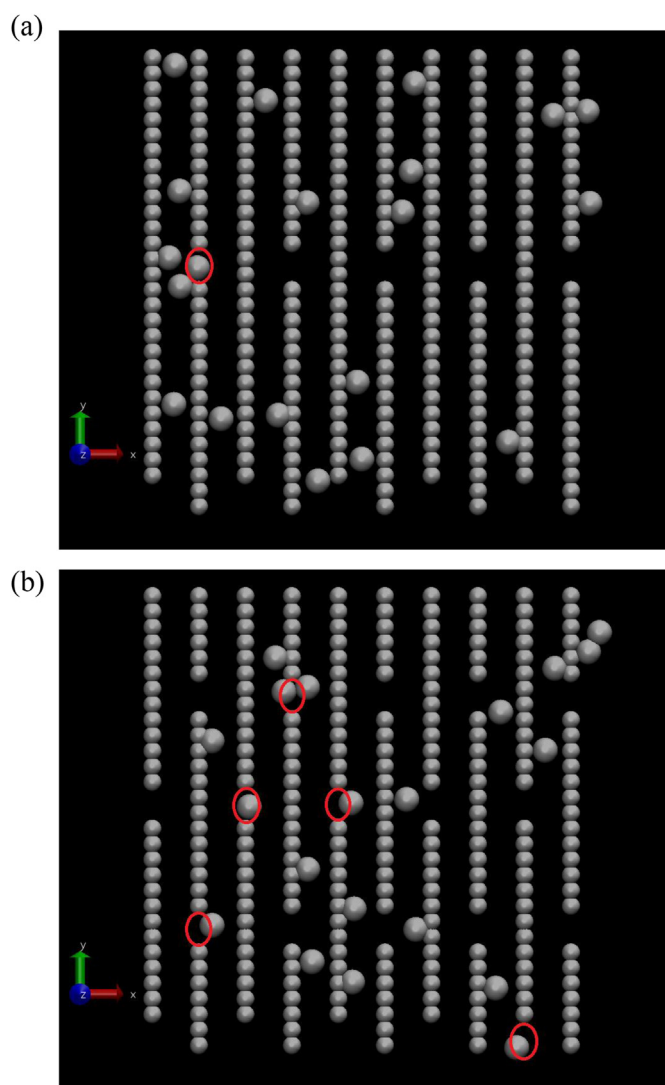


Fig. 3. Simulation snapshots of particles diffusing in 2D array of carbon walls with (a) 1 hole and (b) 2 holes. The widths of both hole and channel are 1.02 nm . Particles crossing holes on carbon walls are highlighted by red cycles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

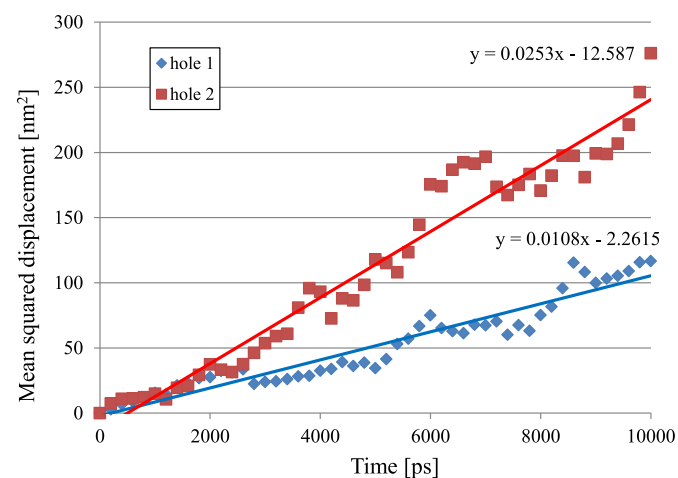


Fig. 4. The X component of mean square displacement for particles diffusing in 2D array of carbon walls with 1 and 2 holes. Linear regression is used to fit MSD curves in the range of $0\text{--}10^4\text{ ps}$.

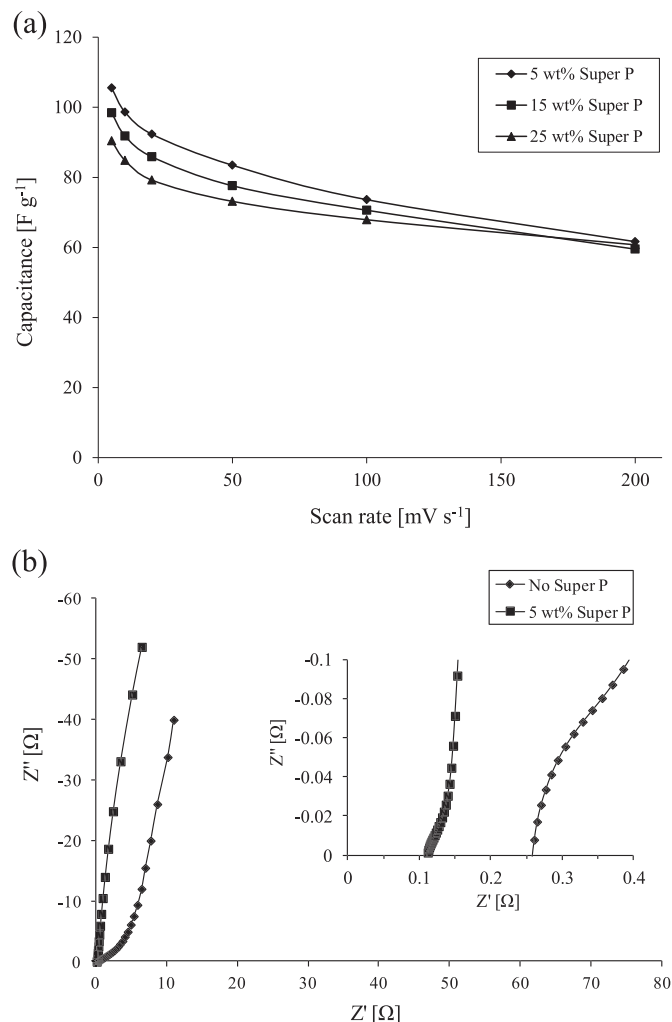


Fig. 5. (a) Capacitance and (b) impedance analysis of supercapacitor with graphene electrodes containing different fractions of conductive agent. The cell capacity is calculated from integrating cyclic voltammograms in the range of 0–1 V at various scan rates. For cyclic voltammetry, loadings of conductive agent Super P in graphene electrode are 5 wt%, 15 wt%, and 25 wt%, respectively. For impedance measurement, a comparison of internal resistance is made between electrodes of pure graphene and graphene mixture with 5 wt% Super P.

conductivity of graphene is potentially attributed to both incomplete reduction during synthesis procedure and insufficient inter-layer contact between crumpled graphene sheets. The exfoliation of graphene upon microwave radiation occurs suddenly, accompanied by the rapid release of gases from some surface areas of graphite oxide. Further microwave treatment results in burning of carbon materials. Further reduction is therefore expected to enhance conductivity of graphene, while restacking of graphene layers should be carefully avoided in order to maintain its porous framework. For commercial electric double-layer capacitor, phenol resin based activated carbons RP20 is commonly adopted due to its high surface area of $1700 \text{ m}^2 \text{ g}^{-1}$ and excellent electrochemical property [28]. Although graphene powder has a much lower surface area than that of RP20, both materials show similar capacitance curves with a maximum of 110 F g^{-1} as seen in Fig. 6. Impedance measurement indicates an identical resistance of 0.11Ω for both materials. Neglecting the mass transfer issue at the low scan rate, the capacity data implies that graphene probably has an internal surface area as large as RP20 for ion adsorption at working conditions. This fact supports our conclusion that graphene

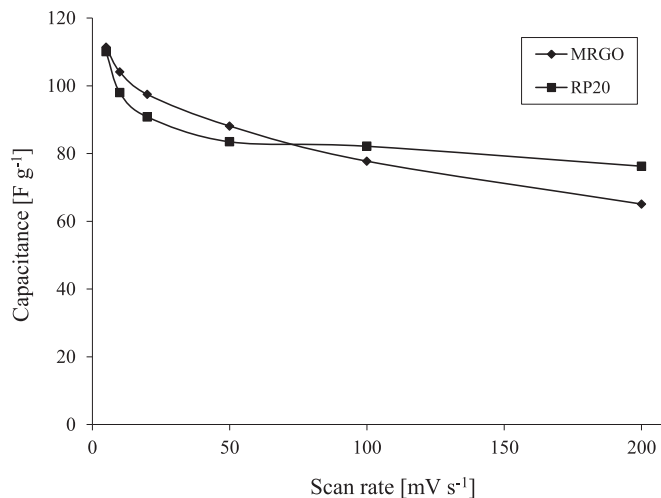


Fig. 6. Capacitance of supercapacitor with electrodes using graphene and activated carbon RP20. The cell capacity is calculated by integrating cyclic voltammograms in the range of 0–1 V at various scan rates.

aggregates may reorganize and optimize its porous structure in response to intercalation of ions and immergence of electrolyte solvent, and consequentially larger accessible surface is exposed for charge storage.

4. Conclusions

In this work, the charge storage mechanism of graphene-based supercapacitor is deeply analyzed using a series of electrochemical measurements in association with molecular simulation. It was found that poor mass transfer and low conductivity are two major factors responsible for the low performance of graphene-based supercapacitor. Molecular simulation was jointly conducted to further investigate charge diffusion phenomenon, and confirmed that the 2D confinement imposed by graphene layers could largely impede the penetration of electrolyte ions to electrode interior. In particular, the in-plane diffusivity of electrolyte ions through graphene electrode may be one order of magnitude slower than that along graphene plane. Innovation of capacitor structures or creation of diffusion paths is expected to generally enhance the electrochemical performance of graphene-based energy storage devices. In other aspect, by implementing the complicated surface chemistry and structure of graphene aggregates, it is possible to use similar simulation methods to investigate molecular transportation through graphene membranes that have been recently proved to have an exceptional performance for gas separation and water purification. In comparison to commercial activated carbon, similar capacitance could be achieved by graphene even with a moderate surface area. It is hypothesized that graphene aggregates may adaptively reorganize and optimize its porous structure in response to intercalation of ions and immergence of electrolyte solvent. As a consequence, a significant amount of initially inaccessible surface of graphene becomes exposed for charge storage under working conditions of supercapacitor. This mechanism is related to the origin of superior electrochemical performance of graphene materials, a fundamental issue for innovative design of graphene-based energy storage devices.

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