Hindawi Publishing Corporation
International Journal of Electrochemistry
Volume 2015, Article ID 801217, 6 pages
http://dx.doi.org/10.1155/2015/801217

Research Article

Investigation of Imbalanced Activated Carbon Electrode Supercapacitors

Tieshi He,[1,2] Xue Ren,[1] Junping Nie,[1] Jun Ying,[1] and Kedi Cai[1,3]

[1] *School of Chemical & Chemical Engineering, Bohai University, Jinzhou 121013, China*
[2] *School of Materials Science & Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0295, USA*
[3] *Interfacial Molecular Spectroscopy Group, Fritz-Haber-Institute of the Max Planck Society, 14195 Berlin, Germany*

Correspondence should be addressed to Tieshi He; hetieshi@163.com and Kedi Cai; caikedihit@126.com

Received 17 October 2015; Accepted 15 December 2015

Academic Editor: Abel C. Chialvo

Imbalanced supercapacitor was constructed by using various ratio of activated carbon (AC) of positive to negative electrode. The electrochemical behavior of imbalanced supercapacitor was investigated using 1.0 M spiro-(1,1′)-bipyrrolidinium tetrafluoroborate electrolyte in propylene carbonate. The results showed that there are some factors that influenced the imbalanced supercapacitor with different AC ratio of positive to negative electrode, the utilization of AC, electrode potential distribution, and life cycle. The imbalanced supercapacitor with an AC weight ratio of 80 : 120 of positive to negative electrode has an average potential distribution in each electrode, and it revealed the best electrochemical performance: specific capacitor was 39.6 $F{\cdot}g^{-1}$, while the charge-discharge efficiency was 97.2% after 2000 life cycle tests.

1. Introduction

Supercapacitor is an electrochemical device in which the charge storage is primarily electrostatic and occurs within the electrochemical double layers (EDLs) [1]. Supercapacitors feature higher specific power upon both charge and discharge and intrinsically lower specific energy than galvanic cells due to the lack of a bulk contribution to charge storage. Supercapacitor with excellent power densities and suitable energy densities is necessary for dynamical power source of electric vehicle [2]. Activated carbon (AC) displays high specific surface (~2000 $m^2{\cdot}g^{-1}$), good electrochemical stability, and environment-friendly property [3]. Hence, AC is a good candidate of current electrode material for supercapacitor [4].

The positive and negative electrodes of AC electrode supercapacitors are composed of the same carbon material (balance capacitors). However, the cations and anions of the electrolyte, which are, respectively, adsorbed on the surfaces of negative and positive electrodes, usually have different sizes, particularly those derived from nonaqueous electrolytes; for example, the cation of spiro-(1,1′)-bipyrrolidinium is 0.371 nm in size and the anion ratio of tetrafluoroborate is 0.229 [5]. The negative and positive carbon electrodes would exhibit different pore structure and surface area requirements to allow the generation of electric double layers on adsorption. Different pore structures and specific surface area are employed to form the electric double layers on the surface of AC for the electronic charge store, and the utilization of AC for the electric double layer forming is also different. Moreover, the ratio of potential assignment between positive electrode and negative electrode has a significant influence on electrolyte degradation [6]. According to $Q = C^+V^+ = C^-V^-$ (Q is the electric quantity, C is the capacitor, and V is potential), the active material content of positive electrode and negative electrode is inversely proportional to its voltage distribution [7]. However, most supercapacitors' positive and negative electrodes were composed of the same mass AC material [8]. In order to maximize the specific interfacial area between the electrode and the electrolyte, the AC mass ratio of the electrode plays a key role in the utilization of AC and life cycle of supercapacitor. The principle of an EDLC is based on the adsorption of electrolyte ions and on the formation of electric double layers on the surface of the electrodes (electrode/electrolyte interface), so

Table 1: Utilization efficiency of activated carbon.

AC mass ratio of electrode (positive : negative)	Measured values (anode : cathode)		Utilization ratio (%)	
	Voltage ratio	Capacity ratio	Positive	Negative
1 : 0.625 (80 : 50 = 1.6)	0.7 V : 2.0 V	1 : 0.35	100	56
1 : 1 (80 : 80 = 1)	1.0 V : 1.7 V	1 : 0.58	100	58
1 : 1.5 (80 : 120 = 0.66)	1.4 V : 1.3 V	1 : 1	100	62
0.44 : 1 (80 : 180 = 0.44)	2.2 V : 0.5 V	0.22 : 1	50	100

the smaller ionic volume will store more electronic energy. In order to improve the specific capacitor of imbalanced supercapacitor, the spiro-(1,1′)-bipyrrolidinium with smaller ionic volume compared to the tetraethylammonium was selected as the electrolyte [9].

In the present work, imbalanced supercapacitors have been constructed using various AC content ratio of positive electrode to negative electrode in nonaqueous electrolytes. The relationship between AC electrode mass ratio and electrode potential distribution, utilization of AC, and life cycle was studied in order to achieve the high specific capacitor and long life cycle of supercapacitor with optimal AC content ratio of positive electrode to negative electrode.

2. Experiment

The supercapacitor used in the investigations is AC (YP50, Kuraray Chemical, Japan) electrodes. Self-supporting electrode sheets based on 80% AC, 10% acetylene black, and 10% polytetrafluoroethylene (PTFE) (from a 50% (w/w) aqueous dispersion, Sigma-Aldrich) as binder were prepared. A dispersion of YP50 and the proper amount of PTFE and acetylene black were stirred vigorously and heated until a dough-like mass was obtained, which was then repeatedly rolled into sheets of different thicknesses (50, 80, 120, and 180 μm). AC electrodes with four different thicknesses (50, 80, 120, and 180 μm) were selected as the negative electrode; an AC electrode with a uniform thickness (80 μm) was used as positive electrode and marked with $r = 80:50$, $r = 80:80$, $r = 80:120$, and $r = 80:180$. The 1.0 mol/L spiro-(1,1′)-bipyrrolidinium tetrafluoroborate in propylene carbonate (SBP-BF_4/PC) was used as the electrolyte.

Electrochemical measurements were performed in a three-electrode disc-type capacitor and the silver wires served as the pseudo-reference electrode [10], in which a separator was soaked in 200 mL of 1.0 mol·L^{-1} of SBP-BF_4/PC electrolyte. The experiments were performed in a three-electrode arrangement with assembled cells dried at 120°C for 24 h, filled, and hermetically sealed in an Ar-filled glove box (H_2O and O_2 <1 ppm). The life cycle test was conducted either at a constant current of 20 mA·g^{-1} or at a voltage within the range 0.0 V–2.7 V. The measured capacitance was expressed in the charge stored (F) per total mass of carbon (g) units (F·g^{-1}).

3. Results and Discussion

The relationship between AC mass ratio and potential distribution of imbalanced supercapacitor was investigated by using galvanostatic charging-discharging test, as shown in Figure 1. According to $Q = C^+V^+ = C^-V^-$, the electrode potential would be inverse ration to electrode capacity, and the electrode capacity would be direct ration to the AC content of electrode. But the capacity calculated is not direct ration to the AC mass content of the electrode which is due to the cations being larger than the volume of the anions in electrolyte; hence, the positive electrode could store more ions than that of the negative electrode for the formation of electric double layers under the same mass AC content. The utilization of AC is calculated via the proportion of the ratio of capacitor measured to the mass ratio of AC positive electrode to negative electrode, as shown in Table 1. The utilization of AC in positive electrode is improved while the AC mass ration of positive electrode to negative electrode increased. The utilization of AC in negative electrode is on the contrary, as shown in Figure 2. The supercapacitor with AC mass ratio $r = 80:120$ shows the highest whole utilization of AC in positive and negative electrode.

Figure 3 shows the cyclic voltammetry curve of the supercapacitor with different r within 2.0 V–3.2 V. A low or high r leads to high potential distribution ratio between the positive electrode and the negative electrode (Figure 1 and Table 1). The imbalanced electrodes lead to imbalanced voltage distribution, such that one electrode exceeds the equivalent square well at lower device potentials resulting in current loss to electrochemical breakdown of the electrolyte [11]. The electrochemical stability of electrolyte decreases with increasing electrode potential, so the stability of working potential window of supercapacitor is less than 3.0 V (Figures 3(a), 3(b), and 3(d)). The supercapacitor with $r = 80:120$ has a wider working potential widow than that of others because the potential distribution of the positive and negative electrodes is almost equal (Figure 1(c) and Table 1); hence, the electrochemical stability of electrolyte was improved, and the maximum specific capacity was also obtained because of its high utilization of electrode-activated materials (Figure 2).

Figure 4 shows the galvanostatic charge-discharge curve of supercapacitor with various AC mass ratios within 2.4 V to 3.2 V, whereas Figure 5 presents the charge-discharge efficiency ($\eta = Q_{dis}/Q_{cha}\%$) of the supercapacitor with

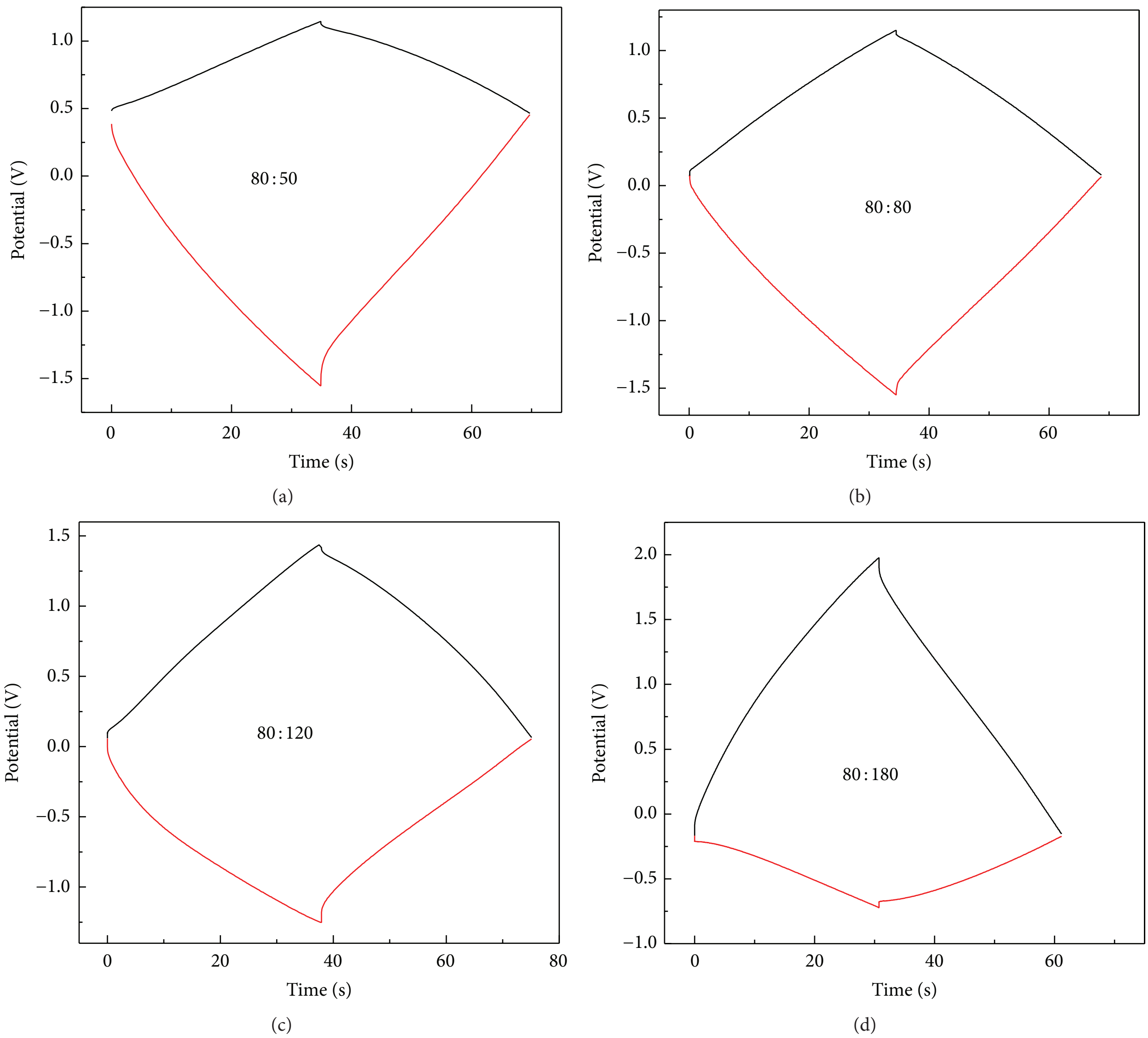

FIGURE 1: Galvanostatic charging-discharging cures. (a) $r = 80:50$. (b) $r = 80:80$. (c) $r = 80:120$. (d) $r = 80:180$.

different AC mass ratios of positive electrode to negative. The η of AC electrode supercapacitor with the imbalanced potential distribution declined sharply when increasing working voltage (Figures 5(a), 5(b), and 5(d)); however, the η of AC electrode supercapacitor with average potential distribution ($r = 80:120$) has little decrease when increasing working voltage (Figure 5(c)), due to the increase of the voltage-difference [12].

The 2000 cycles of charging/discharging tests of the imbalanced supercapacitor were conducted at chronopotentiometry mode in 100 mA within 0.0 V–2.7 V (Figure 6). The specific capacitor of supercapacitor decreases obviously, which is due to the formation of polymer passive films on the surface of AC under electrochemical condition [13]. The passive films blocked the ion entering of the pore and then reduced the formation efficiency of electric double layers especially the micropore and mesopore. The supercapacitors using $r = 80:50$, $r = 80:80$, and $r = 80:180$ show low cycling stability, specifically a high negative electrode potential (Figures 6(a) and 6(b)). The high negative electrode potential improves the reactivity of the solvent in active sites of AC surface, and then the rate of formation of polymer passive films increases on the surface of AC, whereas the specific capacity, charging/discharging efficiency, and life cycle of supercapacitor decrease sharply. The supercapacitor with $r = 80:120$ shows good electrochemical performance because of the high AC utilization, which leads to a higher specific capacity, and the average potential distribution in positive and negative electrodes that decreases the deterioration of electrolyte [14]. Its specific capacitor is 39.6 $F{\cdot}g^{-1}$, and the charge-discharge efficiency is 97.2% after 2000 cycles of charging/discharging (Figure 6(c)).

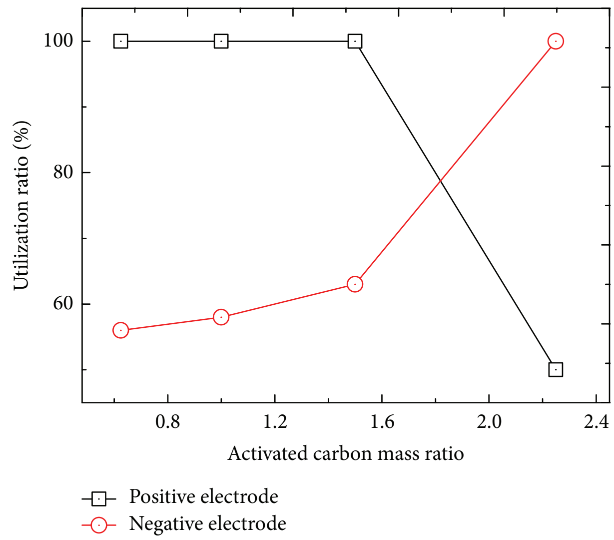

FIGURE 2: Relation between utilization and mass ratio of AC.

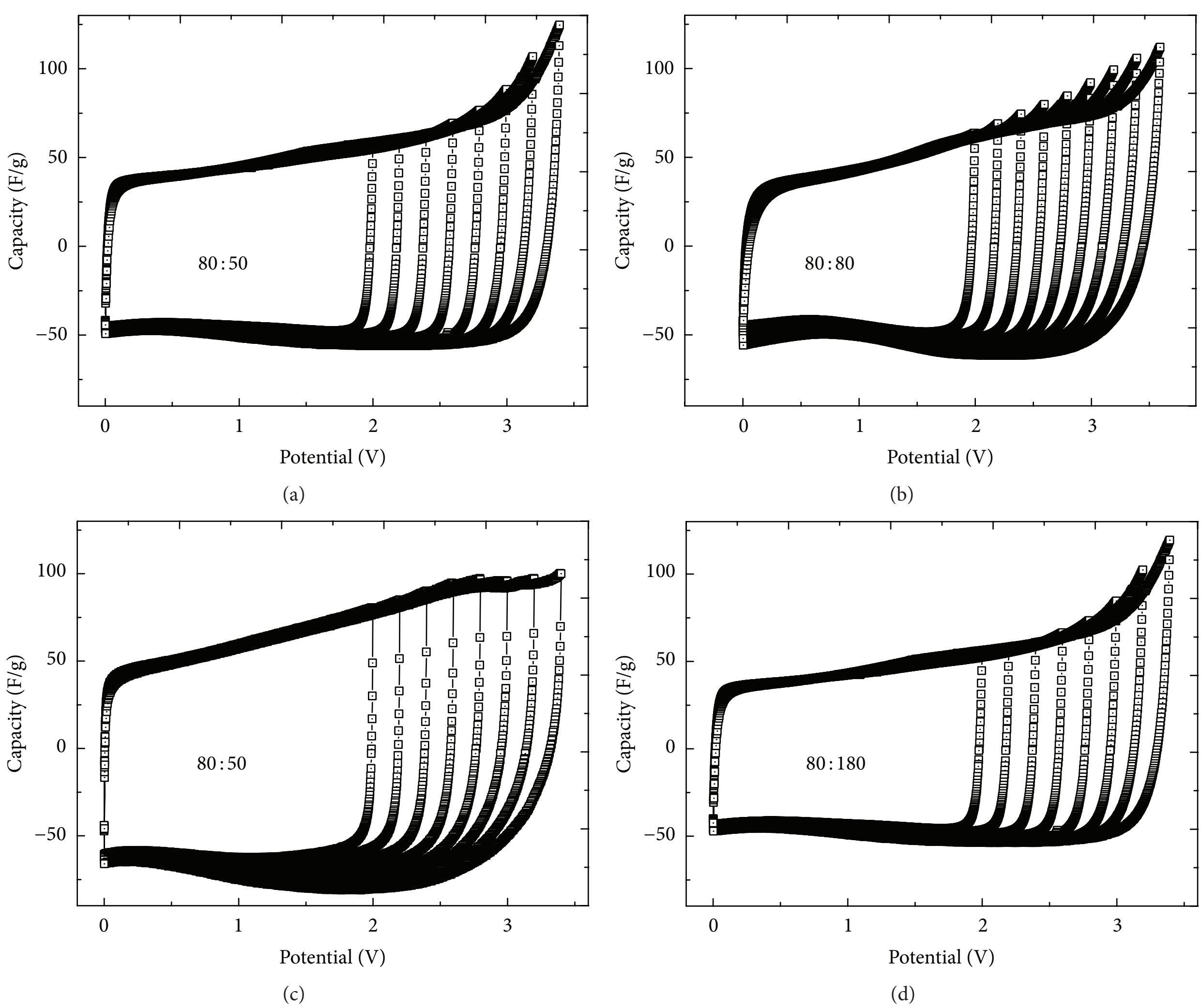

FIGURE 3: Cyclic voltammetry cures. (a) $r = 80:50$. (b) $r = 80:80$. (c) $r = 80:120$. (d) $r = 80:180$.

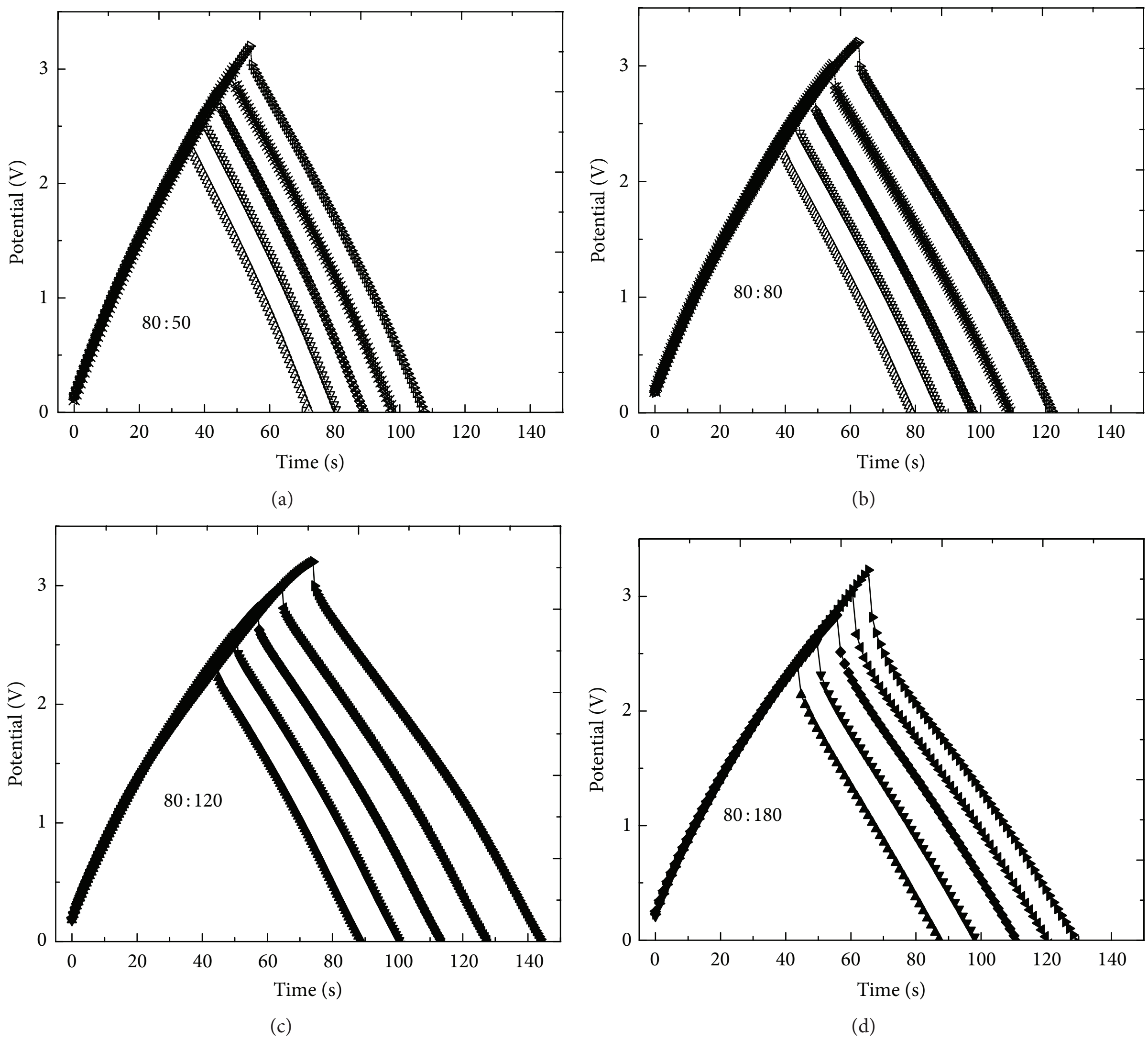

Figure 4: Galvanostatic charge-discharge cures. (a) $r = 80:50$. (b) $r = 80:80$. (c) $r = 80:120$. (d) $r = 80:180$.

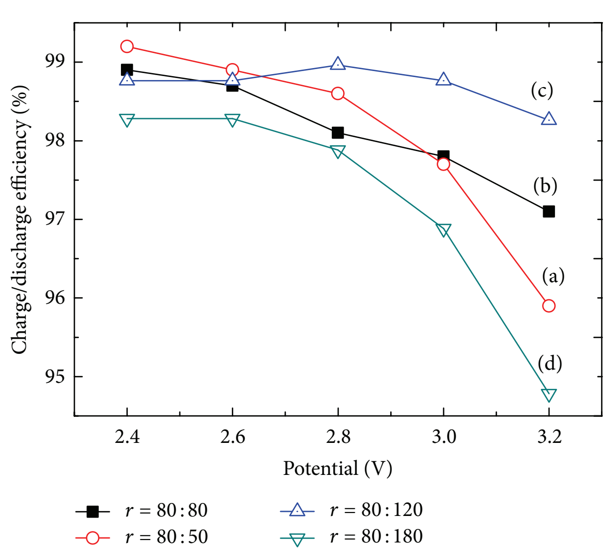

Figure 5: Charge-discharge efficiency cures of different potential. (a) $r = 80:50$. (b) $r = 80:80$. (c) $r = 80:120$. (d) $r = 80:180$.

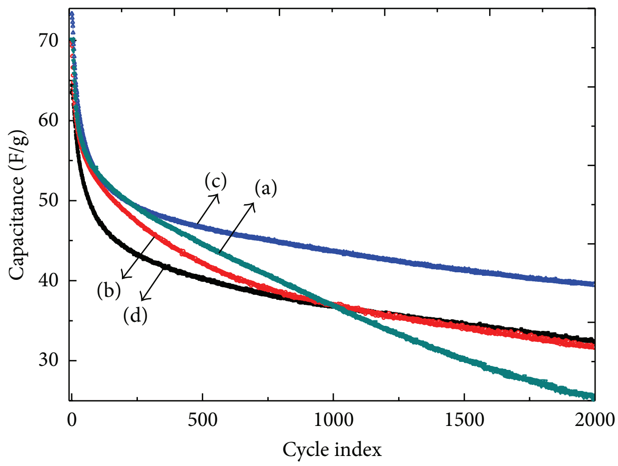

FIGURE 6: Life cycle plot. (a) $r = 80:50$. (b) $r = 80:80$. (c) $r = 80:120$. (d) $r = 80:180$.

4. Conclusion

The potential distribution changes with the AC mass ratio between positive electrode and negative electrode and the distribution of capacity measured are not exactly direct ratio to the AC. The imbalanced supercapacitor with AC mass ratio of positive electrode and negative electrode of 80 : 120 shows the average potential distribution between positive electrode and negative electrode and best electrochemical performance: the specific capacitor is 39.6 $F \cdot g^{-1}$ and charge-discharge efficiency is 97.2% after 2000 times cycles of charging/discharging.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The project is supported by the Higher Education Institutions of Liaoning Province of China (no. L2012398), National Natural Science Foundation of China (no. 21206083), and the Excellent Talents of Liaoning Province of China (no. LR2014033).

References

[1] D.-W. Wang, F. Li, Z.-S. Wu, W. Ren, and H.-M. Cheng, "Electrochemical interfacial capacitance in multilayer graphene sheets: dependence on number of stacking layers," *Electrochemistry Communications*, vol. 11, no. 9, pp. 1729–1732, 2009.

[2] Y. Zhu, S. Murali, M. D. Stoller et al., "Carbon-based supercapacitors produced by activation of graphene," *Science*, vol. 332, no. 6037, pp. 1537–1541, 2011.

[3] A. Jänes, H. Kurig, and E. Lust, "Characterisation of activated nanoporous carbon for supercapacitor electrode materials," *Carbon*, vol. 45, no. 6, pp. 1226–1233, 2007.

[4] C. Zheng, L. Qi, M. Yoshio, and H. Wang, "Cooperation of micro- and meso-porous carbon electrode materials in electric double-layer capacitors," *Journal of Power Sources*, vol. 195, no. 13, pp. 4406–4409, 2010.

[5] H. Wang and M. Yoshio, "Feasibility of quaternary alkyl ammonium-intercalated graphite as negative electrode materials in electrochemical capacitors," *Journal of Power Sources*, vol. 200, no. 1, pp. 108–112, 2012.

[6] S. Ishimoto, Y. Asakawa, M. Shinya, and K. Naoi, "Degradation responses of activated-carbon-based EDLCs for higher voltage operation and their factors," *Journal of the Electrochemical Society*, vol. 156, no. 7, pp. A563–A571, 2009.

[7] P. W. Ruch, D. Cericola, A. Foelske, R. Kötz, and A. Wokaun, "A comparison of the aging of electrochemical double layer capacitors with acetonitrile and propylene carbonate-based electrolytes at elevated voltages," *Electrochimica Acta*, vol. 55, no. 7, pp. 2352–2357, 2010.

[8] L. Wang, M. Toyoda, and M. Inagaki, "Performance of asymmetric electric double layer capacitors—predominant contribution of the negative electrode," *Adsorption Science and Technology*, vol. 26, no. 7, pp. 491–500, 2008.

[9] R. Chandrasekaran, M. Koh, A. Yamauchi, and M. Ishikawa, "Electrochemical cell studies based on non-aqueous magnesium electrolyte for electric double layer capacitor applications," *Journal of Power Sources*, vol. 195, no. 2, pp. 662–666, 2010.

[10] P. W. Ruch, D. Cericola, M. Hahn, R. Kötz, and A. Wokaun, "On the use of activated carbon as a quasi-reference electrode in non-aqueous electrolyte solutions," *Journal of Electroanalytical Chemistry*, vol. 636, no. 1-2, pp. 128–131, 2009.

[11] F. P. Campana, M. Hahn, A. Foelske, P. Ruch, R. Kötz, and H. Siegenthaler, "Intercalation into and film formation on pyrolytic graphite in a supercapacitor-type electrolyte $(C_2H_5)_4NBF_4$/propylene carbonate," *Electrochemistry Communications*, vol. 8, no. 8, pp. 1363–1368, 2006.

[12] K. Xu, M. S. Ding, and T. R. Jow, "Quaternary onium salts as nonaqueous electrolytes for electrochemical capacitors," *Journal of the Electrochemical Society*, vol. 148, no. 3, pp. A267–A274, 2001.

[13] X. Yu, D. Ruan, C. Wu, J. Wang, and Z. Shi, "Spiro-(1,1′)-bipyrrolidinium tetrafluoroborate salt as high voltage electrolyte for electric double layer capacitors," *Journal of Power Sources*, vol. 265, pp. 309–316, 2014.

[14] B. Fang, Y.-Z. Wei, and M. Kumagai, "Modified carbon materials for high-rate EDLCs application," *Journal of Power Sources*, vol. 155, no. 2, pp. 487–491, 2006.