

Short Communication

Synthesis of a Highly Porous Nitrogen-Doped Carbon Material from a Melamine/Formaldehyde Resin with Potassium Citrate

Wei Xiong, Ji Hoon Kang, Jin Kyeong Kang, and Yongju Jung*

Department of Chemical Engineering, Korea University of Technology and Education (KOREATECH), Cheonan, 330-780, Korea

*E-mail: yjung@koreatech.ac.kr

Received: 3 July 2017 / *Accepted:* 12 August 2017 / *Published:* 12 September 2017

Nitrogen-doped porous carbons were synthesized from an aqueous solution of melamine and formaldehyde. The addition of potassium citrate to the solution mixture led to a tremendous increase in the surface area from 74 m²/g to 2718 m²/g, indicating that potassium citrate served as an excellent pore former. The nitrogen-doped carbon exhibited remarkable capacitive performance, such as a high capacitance of 320 F/g at 0.1 A/g, an excellent rate capability (70 % at 10.0 A/g), and a high cycling stability (94.6 % retention after 2000 cycles) in 6.0 M KOH aqueous solution. Furthermore, the nitrogen-doped carbon delivered a high energy density of 7.8 Wh/kg even at a high power density of 5000 W/kg. We believe that the synthesis strategy presented in this work could be used as a promising way to fabricate electrode materials for high-performance supercapacitors.

Keywords: Melamine, Formaldehyde, Potassium Citrate, N-doped Porous Carbon

1. INTRODUCTION

Nitrogen-doped porous carbon materials for supercapacitor applications have attracted much attention from researchers worldwide. This is because nitrogen functional groups improve the surface wettability of carbon electrodes against electrolyte solutions and provide additional pseudo-capacitance[1-3]. Many N-containing polymers have been widely used as carbon precursors to prepare N-doped porous carbons[4,5]. A melamine/formaldehyde resin with a high nitrogen content is one of the most common carbon precursors. However, in general, the surface area of N-doped carbons prepared from the melamine/formaldehyde resin is not large enough to allow the fabrication of high-performance supercapacitor electrodes[6,7]. To address this issue, copious approaches have been presented, including a conventional activation process with a KOH solution[8,9] and template replica methods[10,11]. Porous carbons with well-defined nanostructures have been synthesized via nano-

replication methods. However, these methods composed of several steps are tricky and cumbersome, which hinders their practical implementation. Recently, it was reported that porous carbons with large surface areas can be easily made through the direct carbonization of potassium citrate [12-15]. Inorganic species, such as K_2CO_3 and K_2O , those generated during carbonization, were found to serve as activating agents.

In this work, we present a new synthesis approach to fabricate N-doped porous carbons with large surface areas by incorporating the pore forming agent potassium citrate into the melamine/formaldehyde resin. We assumed that porous carbon with a well-defined nanostructure could be achieved by uniformly distributing potassium citrate within a carbon precursor structure, as illustrated in Fig. 1.

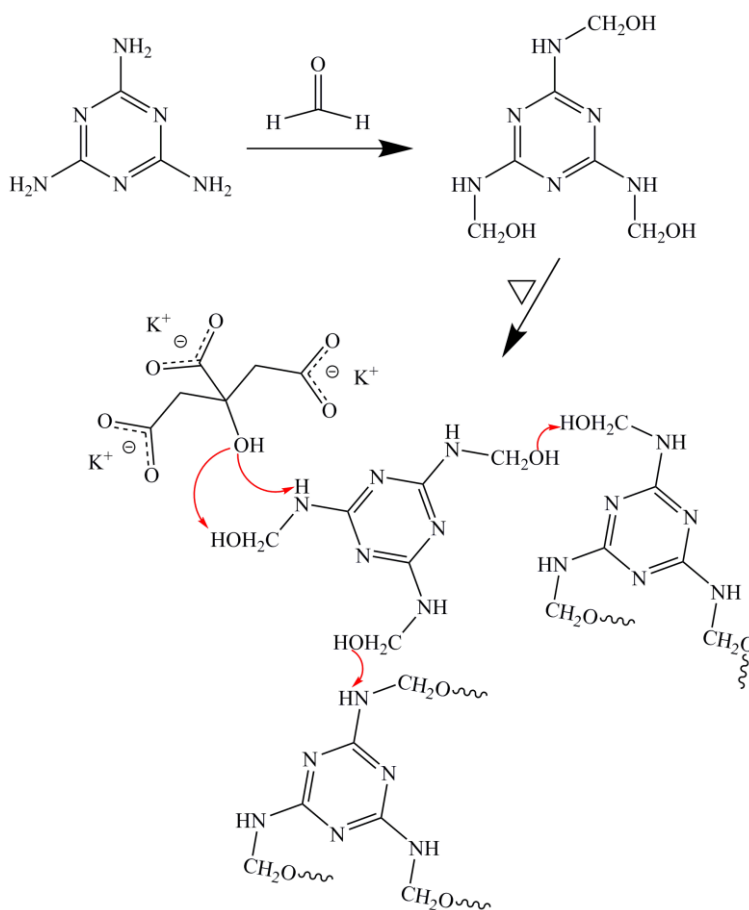


Figure 1. Chemical interaction between the melamine/formaldehyde resin and potassium citrate.

2. EXPERIMENTAL SECTION

Melamine (3.78 g, 99 %, Sigma-Aldrich) and 7.1 g of a formaldehyde solution (~38 %, Sigma-Aldrich) were mixed in 10 mL of distilled water and stirred at 80 °C for 30 min. After adding 9.72 g of potassium citrate, the mixture solution was heated for 1 h. Then, the resulting sample was dried at 100 °C for 24 h, followed by carbonization at 850 °C for 2 h under an inert argon atmosphere. The resultant carbon product, denoted as MF-NC-K, was washed several times with distilled water to remove

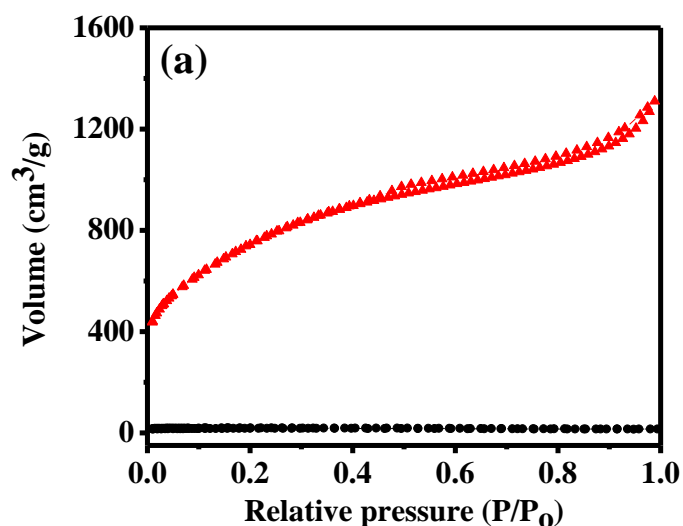
impurities, such as the inorganic salts. Subsequently, it was dried at 150 °C for 6 h. For comparison, a control sample, denoted as MF-NC, was prepared from the melamine/formaldehyde resin without potassium citrate using the same process.

The microstructures of the porous carbons were examined by N₂ adsorption tests (Tristar II 3020, Micromeritics). Brunauer-Emmett-Teller (BET) and Barret-Johner-Halenda (BJH) methods were used to estimate the specific surface areas and the pore size distributions, respectively. The nitrogen contents of the carbons, measured by elemental analysis (Flash EA2000 analyser, Thermo, UK), were observed to be less than 7 wt%.

All electrochemical measurements were tested in a coin-type cell with a 6.0 M KOH electrolyte solution. A slurry comprising 80 wt% porous carbon, 10 wt% polytetrafluoroethylene binder, and 10 wt% acetylene black was dispersed in isopropyl alcohol. The resultant slurry was coated onto a Ni mesh to fabricate the carbon electrode to be punched out into circular disks (2 cm²) and dried at 100 °C before cell assembly. Coin cells were assembled with two identical carbon electrodes and a glass fiber membrane separator. Cyclic voltammetry and charge-discharge tests were carried out in a voltage range from -1.0 to 0.0 V. The charge-discharge tests were performed at a current density of 0.1 to 10 A/g.

3. RESULTS AND DISCUSSION

Fig. 2a shows the nitrogen adsorption isotherm curves of the two nitrogen-doped carbon samples synthesized from melamine/formaldehyde resins. The nitrogen adsorption characteristics were profoundly affected by the addition of potassium citrate. The N-doped carbon prepared with potassium nitrate (MF-NC-K) exhibited a combined type-I and type-IV isotherm with a hysteresis loop at a relative pressure of ~0.5 to 0.9, suggesting the existence of micro- and mesopores[16-19].



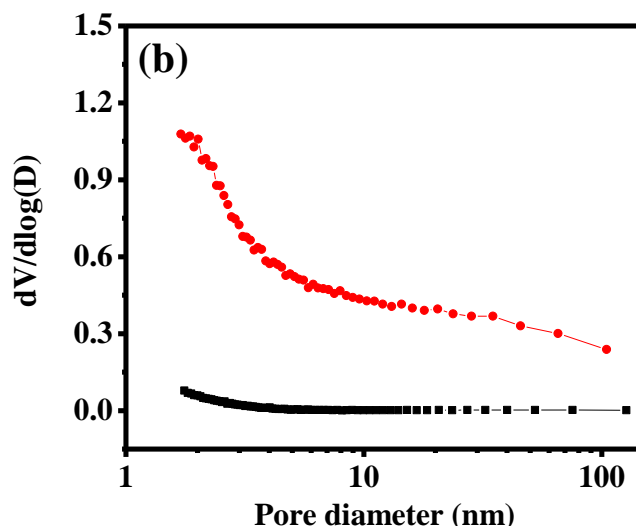


Figure 2. (a) N_2 sorption isotherms and (b) pore size distribution curves of MF-NC (—) and MF-NC-K (---).

It was reported that potassium citrate can contribute to the formation of nanostructured carbons with abundant pores through the following two routes: (1) the reaction of CO_2 and K_2O , the decomposed products of potassium citrate, with carbon and (2) the in situ generation of pore-forming agents, such as CO gas and K vapor[17]. As potassium citrate was incorporated into the resin, the surface area of carbon sample remarkably increased from $74 \text{ m}^2/\text{g}$ to $2718 \text{ m}^2/\text{g}$, along with a considerable increase in the total pore volume from 0.03 to $2.02 \text{ cm}^3/\text{g}$ (Table 1). Therefore, this indicates that potassium citrate induced well-developed pore structures within the nitrogen-doped carbon frameworks.

Table 1. The structural characteristics of the nitrogen-doped carbons.

Sample	S_{mi}^a (m^2/g)	S_{BET}^b (m^2/g)	V_{mi}^c (cm^3/g)	V_t^d (cm^3/g)
MF-NC	54	74	0.02	0.03
MF-NC-K	1892	2718	0.92	2.02

^a Micropore surface area.

^b BET surface area calculated in the p/p_0 range of 0.05–0.20.

^c Micropore volume.

^d Total pore volume measured at $p/p_0 = 0.99$.

Fig. 2b shows the pore size distribution of MF-NC-K estimated from the adsorption branch of the N_2 isotherm curve using the BJH method. MF-NC-K possessed a well-developed porous structure with a pore size widely ranging from 2 nm to 100 nm. Interestingly, as the pore diameter increased, the

pore population sharply decreased below 5 nm and gradually decreased in a pore size range of 5 to 100 nm.

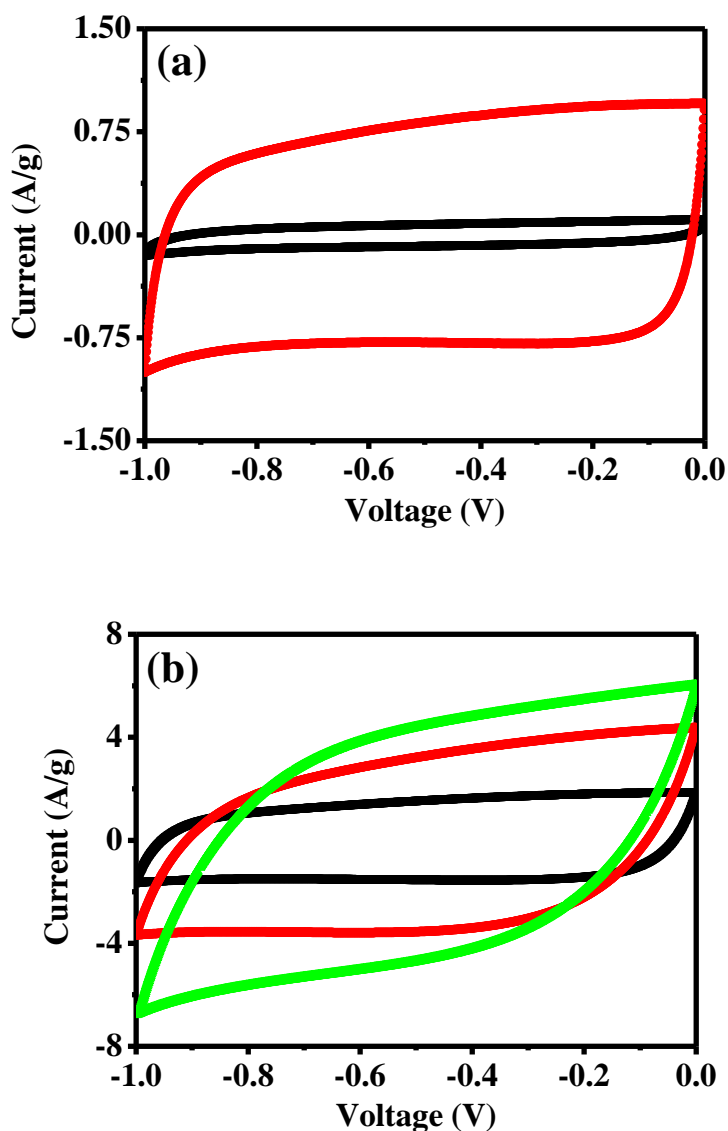


Figure 3. (a) CV curves of the MF-NC (–) and MF-NC-K (–) electrodes at 10 mV/s, and (b) CV curves of the MF-NC-K electrode at 20 (–), 50 (–) and 100 (–) mV/s in 6.0 M KOH solution.

The capacitive performances of the carbon samples were examined in 6.0 M KOH solution using cyclic voltammetry and charge-discharge tests. Both carbon electrodes exhibited typical rectangular CV curves at a scan rate of 10 mV/s (Fig. 3a), demonstrating that they operated normally as supercapacitors. Overall, compared to MG-NC, MF-NC-K showed remarkably enhanced capacitive performance, as evidenced by the integrated area of the CV curves[20,21]. MF-NC-K exhibited curves similar to that of ideal CV curves even at a fast scan rate of 100 mV/s (Fig. 3b). This implies that the charge-discharge process in the MF-NC-K electrode occurred very rapidly.

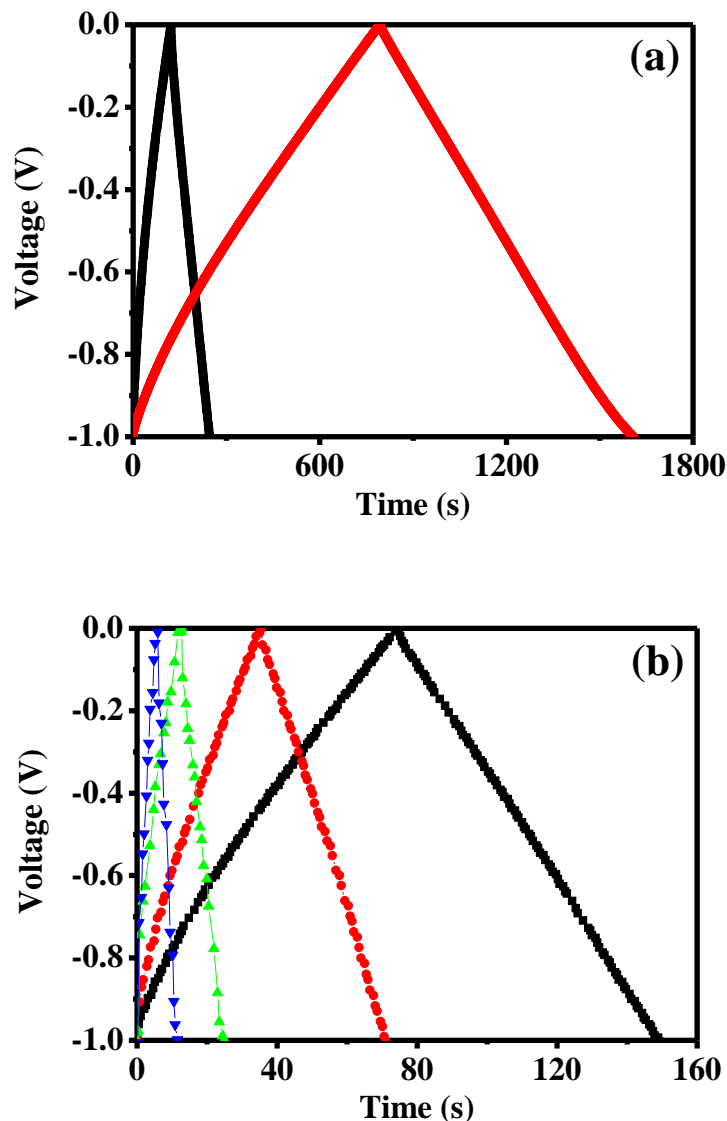


Figure 4. (a) Charge-discharge curves of the MF-NC (–) and MF-NC-K (–) electrodes at 0.1 A/g, and (b) rate capability of MF-NC-K (–) electrode at 1.0 A/g (–), 2.0 A/g (–), 5.0 A/g (–) and 10.0 A/g (–) in 6.0 M KOH solution.

Fig. 4a shows the galvanostatic charge-discharge curves of the carbon samples at a current density of 0.1 A/g. MF-NC-K showed much higher capacitance (320 F/g) with typical triangular charge-discharge curves compared to MF-NC (50 F/g) at a current density of 0.1 A/g. Even at a notably high current density of 10 A/g, MF-NC-K exhibited excellent capacity retention of 70 %, as shown in Fig. 4b, suggesting fast ion transport within the MF-NC-K carbon framework. Indeed, MF-NC-K presented relatively high capacitive performance compared to those of other nitrogen-doped carbons (Table 2). This feature can be mainly attributed to the large surface area of MF-NC-K considering that the nitrogen contents of the carbon materials are very similar.

Table 2. Comparison of the capacitive performances of the nitrogen-doped carbons with those of other porous carbons.

Samples	Capacitance (F/g)					Reference
	0.1 A/g	1.0 A/g	2.0 A/g	5.0 A/g	10.0 A/g	
MF-NC	50	45	-	-	-	This work
MF-NC-K	320	300	282	250	224	This work
NPC			280 at 0.2 A/g			[2]
HPC			275 at 0.125 A/g			[8]
NHPC			257.8 at 0.4 A/g			[10]
NC			223 at 0.2 A/g			[22]
NG			289 at 0.2 A/g			[22]

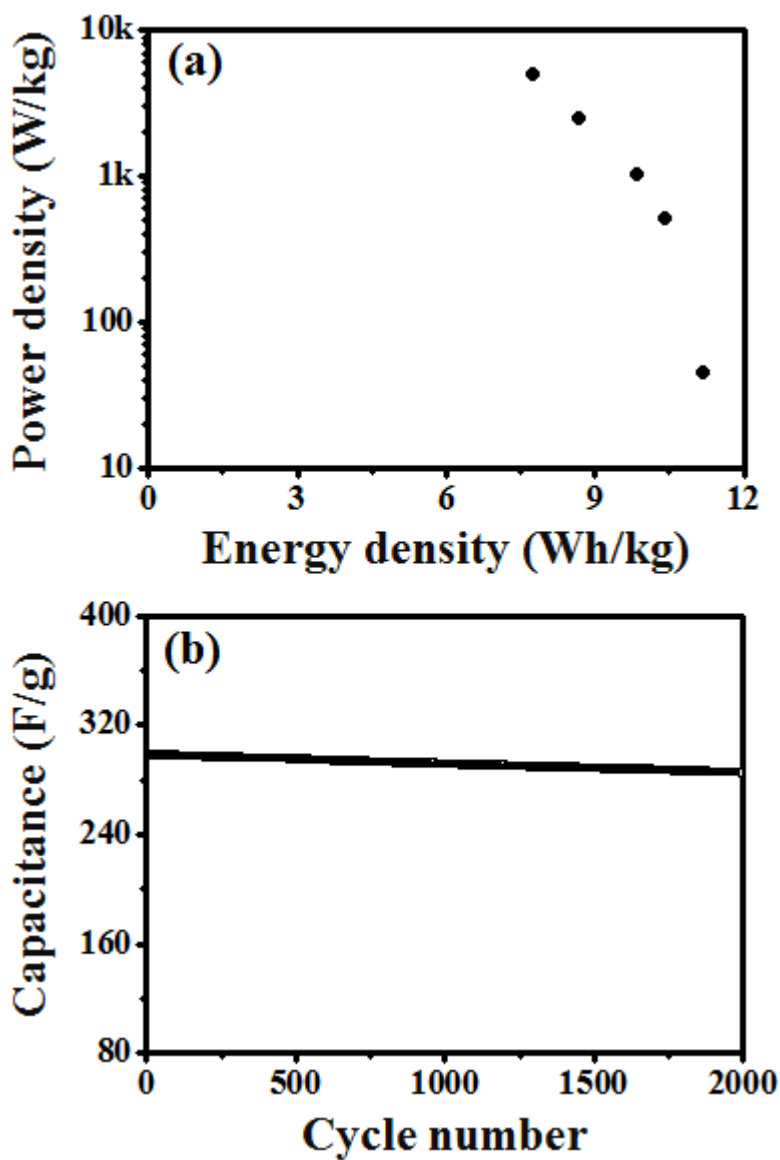


Figure 5. (a) Ragone plot of the MF-NC-K electrode, and (b) cycling performance of the MF-NC-K electrode at 1.0 A/g.

When compared to that of typical non-doped carbon with a considerably large surface area ($3332 \text{ m}^2/\text{g}$), the MF-NC-K electrode showed better electrochemical performance[8]. This feature can be attributed to the pseudo-capacitance induced by doped nitrogen[1-3].

Fig. 5a shows a Ragone plot, which reveals the relationship between the energy and power densities. The MF-NC-K electrode produced a maximum energy density of 11.2 Wh/kg at a power density of 44.8 W/kg . Even at a power density of 5000 W/kg , its energy density was measured to be 7.78 Wh/kg , which is prominently higher than those of other supercapacitors[22-26]. Moreover, the MF-NC-K electrode showed excellent cycling stability (94.6% retention after 2000 cycles) at 1.0 A/g (Fig. 5b). Based on these overall results, we believe that this porous carbon synthesis approach can be widely applied to create high-performance carbon materials.

4. CONCLUSION

We presented a new method to synthesize nitrogen-doped porous carbons using a potassium-citrate-incorporated melamine/formaldehyde resin. Potassium citrate was added to generate nanostructured porous carbon comprising abundant micro- and mesopores. The surface area of the nitrogen-doped carbon was considerably enhanced from $74 \text{ m}^2/\text{g}$ to $2718 \text{ m}^2/\text{g}$ by adding potassium citrate. The nitrogen-doped carbon exhibited a remarkable capacitance of 320 F/g at 0.1 A/g and an excellent rate capability of 70% retention at 10.0 A/g in 6.0 M KOH solution. Furthermore, the nitrogen-doped carbon electrode provided a remarkable energy density of 7.8 Wh/kg at an extremely high power density of 5000 W/kg . We believe that the presented synthesis method can be readily extended to the fabrication of porous carbons using different carbon sources for use as supercapacitor electrode materials.

ACKNOWLEDGEMENTS

This work was supported by the Financial Assistance Programs for Postdoctoral Researchers of KOREATECH.

References

1. X. L. Yu, J. F. Zhao, R. T. Lv, Q. H. Liang, C. Z. Zhan, Y. Bai, Z. H. Huang, W. C. Shen, F. Y. Kang, *J. Mater. Chem. A* 133 (2015) 18400.
2. J. G. Jiang, L. K. Bao, Y. W. Qiang, Y. C. Xiong, J. Y. Chen, S. Y. Guan, J. D. Chen, *Electrochim. Acta* 158 (2015) 229.
3. J. Z. Chen, J. L. Xu, S. Zhou, N. Zhao, C. P. Wong, *Nano Energy* 25 (2016) 193.
4. X. M. Ma, M. X. Liu, L. H. Gan, Y. H. Zhao, L. W. Chen, *Electrochim. Acta* 194 (2016) 168.
5. L. Wang, Z. Y. Gao, J. L. Chang, X. Liu, D. P. Wu, F. Xu, Y. M. Guo, K. Jiang, *ACS Appl. Mater. Interfaces* 7 (2015) 20234.
6. D. Hulicova, M. Kodama, H. Hatori, *Chem. Mater.* 18 (2006) 2318.
7. C. L. Qin, X. Lu, G. P. Yin, Z. Jin, Q. Tan, X. D. Bai, *Mater. Chem. Phys.* 126 (2011) 453.
8. Y. Gao, W. L. Zhang, Q. Y. Yue, B. Y. Gao, Y. Y. Sun, J. J. Kong, P. Zhao, *J. Power Sources* 270 (2014) 403.

9. F. Barzegar, A. Bello, O. Fashedemi, J. K. Dangbegnon, D. Y. Momodu, F. Taghizadeh, N. Manyala, *Electrochim. Acta* 180 (2015) 442.
10. G. Q. Wang, J. Zhang, S. Kuang, J. Zhou, W. Xing, S. P. Zhuo, *Electrochim. Acta* 153 (2015) 273.
11. J. Tang, J. Liu, R. Salunkhe, T. Wang, Y. Yamauchi, *Chem. Commun.* 52 (2016) 505.
12. M. Sevilla, A. B. Fuertes, *ACS Nano* 8 (2014) 5069.
13. G. A. Ferrero, M. Sevilla, A. B. Fuertes, *Carbon* 88 (2015) 239.
14. H. M. Luo, Y. F. Yang, X. Zhao, J. Q. Zhang, Y. Z. Chen, *Electrochim. Acta* 169 (2015) 13.
15. Y. T. Jiang, J. Yan, X. L. Wu, D. D. Shan, Q. H. Zhou, L. L. Jiang, D. Yang, Z. J. Fan, *J. Power Sources* 307 (2016) 190.
16. M. X. Liu, L. Y. Chen, D. Z. Zhu, H. Duan, W. Xiong, Z. J. Xu, L. H. Gan, L. W. Chen, *Chinese Chem. Lett.* 27 (2016) 399.
17. W. Xiong, G. J. Yang, T. H. Yang, S. T. Liu, Y. J. Jung, *Bull. Korean Chem. Soc.* 38 (2017) 350.
18. M. X. Liu, X. M. Ma, L. H. Gan, Z. J. Xu, D. Z. Zhu, L. W. Chen, *J. Mater. Chem. A* 2 (2014) 17107.
19. W. Xiong, L. Zhou, S. T. Liu, *Chem. Eng. J.* 284 (2016) 650.
20. X. M. Ma, M. X. Liu, L. H. Gan, Y. H. Zhao, L. W. Chen, *J. Solid State Electrochem.* 17 (2013) 2293.
21. J. S. Qian, H. Jin, B. L. Chen, M. Lin, W. Lu, W. M. Tang, W. Xiong, L. Chan, S. P. Lau, J. K. Yuan, *Angew. Chem. Int. Ed.* 54 (2015) 1.
22. M. Li, J. M. Xue, *J. Phys. Chem. C* 118 (2014) 2507.
23. N. Li, T. Lv, Y. Yao, H. L. Li, K. Liu, T. Chen, *J. Mater. Chem. A* 5 (2017) 3267.
24. S. H. Zheng, Z. L. Li, Z. S. Wu, Y. F. Dong, F. Zhou, S. Wang, Q. Fu, C. L. Sun, L. W. Guo, X. H. Bao, *ACS Nano* 11 (2017) 4009.
25. F. Gao, G. H. Shao, J. Y. Qu, S. Y. Lv, Y. Q. Li, M. B. Wu, *Electrochim. Acta* 155 (2015) 201.
26. R. L. Liu, L. Wan, S. Q. Liu, L. X. Pan, D. Q. Wu, D. Y. Zhao, *Adv. Funct. Mater.* 25 (2015) 526.

© 2017 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).