International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

Acidified Activated Carbon with Enhanced Electrochemical Performance for Supercapacitors

Bangmin Gao, Yan Li, Yan Tian, and Ligang Gai*

Institute of Advanced Energy Materials and Chemistry, School of Chemistry and Pharmaceutical Engineering, Qilu University of Technology, Jinan 250353, People's Republic of China *E-mail: <u>liganggai@qlu.edu.cn</u>

Received: 2 November 2016 / Accepted: 29 November 2016 / Published: 12 December 2016

Activated carbons carrying oxygen functional groups have been subjected to extensive research due to their potential applications in adsorption, sensors, catalysis, drug delivery, and energy storage/conversion systems. In this paper, acidified activated carbon (AAC) has been prepared through chemical oxidation of commercial activated carbon (AC) in a mild oxidation environment, providing AAC with enhanced concentration of single-graphene layers, improved degree of graphitization, reduced specific surface area and micropore volume, and a surface dominated by C=O/C–O groups. The electrochemical performance of AC and AAC is investigated in the role of electrode materials for supercapacitors in a three-electrode mode. Compared with AC, AAC exhibits an enlarged working potential window and superior electrochemical performance at current densities lower than 10 A g⁻¹. After 5000 cycles at 1 A g⁻¹, the specific capacity of AAC is retained at126.7 F g⁻¹, higher than that of 113.7 F g⁻¹ for AC.

Keywords: Acidified activated carbon; Chemical oxidation; Oxygen-containing functional groups; Electrode materials; Supercapacitors

1. INTRODUCTION

Carbon materials in forms of activated carbons, diamond, fullerene, carbon nanodots, nanotubes, nanofibres, and graphene have been subjected to extensive research due to their wide applications in water treatment [1], sensors [2], catalysis [3], drug delivery [4], and energy storage/conversion systems [5-12]. Among the carbon materials, activated carbons are the most widely used forms in practical applications because of the large specific surface area (S_{BET}), high porosity, and low cost [1,8-12]. In the case of applications in energy storage/conversion systems, however, crude activated carbons suffer from relatively low specific capacity. For examples, the activated carbon with S_{BET} of 615 m² g⁻¹ exhibits gravimetric capacitance in the range of 18–35 F g⁻¹ for supercapacitors

with organic electrolyte [12]; and high-surface-area nanocellular carbon foams (537.4 m² g⁻¹) serving as anode materials for sodium-ion batteries provide a low specific capacity of 46 mA h g⁻¹ [6]. The relatively large S_{BET} yet small values of specific capacity are attributed to that not all the S_{BET} is electrochemically accessible by the electrolyte [13].

To improve the electrochemical performance of carbonaceous materials, the well-accepted strategy is endowing them with the pseudocapacitive ability by creating surface functional groups, using the methods of doping [14], plasma [15], and chemical oxidation [6,12]. Among the methods, the solution-based chemical oxidation is widely used for post-treatment of the ready-made activated carbons to create oxygen-containing functional groups [6,12]. Although the S_{BET} of the target carbons is usually reduced after chemical oxidation in solution, their electrochemical performance can be greatly enhanced. Taking the reference [12] as an example, the S_{BET} of the target carbon is dramatically reduced to 151 from 615 m² g⁻¹ while the specific capacitance is greatly enhanced to 80–140 from 18–35 F g⁻¹. The enhanced electrochemical performance of the surface-oxidized carbons is attributed to the surface-reaction driven charge storage mechanism involving pseudocapacitive redox reactions on the carbonyl sites [6,12].

On the other hand, the electrochemical performance of the acidified activated carbons is influenced by the concentration of acidic surface groups such as carboxyls [16]. As documented in literature [17], the acidic groups are detrimental to the rate capability and cycling stability of carbonaceous materials. To circumvent the disadvantage of the chemical oxidation, a strategy has been developed to eliminate the acidic surface groups by anneal treatment [16] or gamma-ray irradiation [11]. However, this complicates the synthetic procedure for the surface-modified activated carbons with enhanced electrochemical performance.

In this paper, we report on simple preparation of the surface-modified activated carbon through mild oxidation of a commercial activated carbon (AC) in nitric acid aqueous solution, yielding an acidified activated carbon (AAC) with surface wealthy in C=O and C–O yet scarce of O–C=O groups. The resulting AAC was comparatively investigated with AC in the role of electrode materials for supercapacitors with aqueous electrolyte.

2. EXPERIMENTAL

2.1. Preparation of AAC

Commercial activated charcoal (A.R., Xilong Chemical Engineering Co., Guangdong, China) was used as the original AC. For preparation of AAC, 4 g of AC powders were transferred into a 250 mL of three-mouth flask, followed by addition of 150 mL of 7.2 mol L^{-1} HNO₃. The mixture was magnetically stirred at 80 °C for 6 h and then allowed to cool to room temperature. The resulting AAC was collected by filtration, washed thoroughly with distilled water several times, and finally dried in a vacuum oven. The weight of the resulting AAC is ca. 3.56 g, rendering a weight loss of ca. 11%.

2.2. Characterization

X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å), operating at 40 kV and 40 mA. Raman spectra were collected at room temperature on a Renishaw inVia-Reflex confocal micro-Raman spectrometer with a 633 nm He-Ne probe laser. Fourier transform infrared (FT-IR) spectra were collected on a Shimadzu IRPrestige-21 infrared spectrometer using pressed KBr discs. The FT-IR spectra were recorded with resolution of 4 cm⁻¹ over a range of 4000–400 cm⁻¹. Field-emission Scanning electron microscopy (FE-SEM) images, energy dispersive spectra, and elemental distribution mapping images were taken on a Zeiss SUPRATM 55 field-emission scanning electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher Scientific ESCALAB 250 Xray photoelectron spectrometer, using monochromatic Al K α radiation (1486.6 eV). Binding energies for high-resolution spectra were calibrated by setting C1s at 284.8 eV. Nitrogen sorption isotherms were collected at 77.1 K using a Micromeritics ASAP2020 sorption analyzer. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}). The pore size distribution (PSD) was evaluated by the non-local density functional theory (NLDFT) model assuming slit pores in carbon. Before recording the nitrogen sorption isotherms, the samples were degassed at 200 °C for 12 h.

The conductivity of the samples was measured on a RTS-8 four probe resistivity tester (Guangzhou Four Probe Tech., China). The sample powders were separately mixed with polyvinylidene fluoride (PVDF) in a weight ratio of 9:1 and then pressed under a pressure of 10 MPa to offer discs with diameter of 15 mm and thickness of 0.2 mm.

2.3. Electrochemical test

Electrochemical tests were conducted on a CHI 660E electrochemical workstation (Shanghai CH Instruments Co., China). The electrochemical properties of the samples were evaluated through a three-electrode mode, using cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) techniques.

For the three-electrode system, a platinum sheet was used as the counter electrode, Hg/Hg₂SO₄ electrode as the reference electrode, and 1 mol L^{-1} H₂SO₄ aqueous solution as the electrolyte. The working electrode was prepared by blade-coating well-blended slurry onto a stainless steel cloth, which served as the current collector. The slurry consists of 80 wt.% active material, 10 wt.% Super-P (conductive carbon), and 10 wt.% PVDF in *N*-methyl-2-pyrrolidone. The as-made electrodes were dried in a vacuum oven at 80 °C for 12 h, and then subjected to double rolling to ensure close contact between the active material and the current collector. The mass of active material upon the stainless steel cloth was 2–3 mg, and the coating area was 1 cm².

The voltage windows for the CV and GCD curves were selected at -0.68-0.27 and -0.7-0.4 V vs. Hg/Hg₂SO₄ for AC and AAC, respectively. Alternating current (AC) EIS spectra were collected in a frequency range of $10^{-2}-10^{5}$ Hz at the open circuit voltage with AC amplitude of 5 mV. The

gravimetric capacitance (C_g , F g⁻¹) derived from galvanostatic discharge curves was calculated from eq 1, expressed as [14]:

$$C_{\rm g} = \frac{I\Delta t}{m\Delta V} \quad (1)$$

where I is the constant discharge current (ampere), Δt the discharge time (second), ΔV the voltage window (volts), and m the mass of active material on the working electrode (gram).

3. RESULTS AND DISCUSSION

3.1. Structure, composition, and morphology



Figure 1. XRD spectra of the samples.

Fig. 1 shows the XRD spectra of the samples. The broad diffraction peaks centered at 23.5° and 42.5° correspond separately to the (002) and (100) planes of activated carbons [11,13,18,19]. Compared with that of AC, the peak intensity of the broad diffractions of AAC is increased. This result indicates an enhanced concentration of single-graphene layers [18,19]. As demonstrated in literature [18,19], the empirical *R* value, defined as the ratio of the (002) peak intensity relative to the background at the same scattering angle (R = B/A, Fig. 1), is related to the concentration of single-graphene layers. The sample within a given sample. A lower *R* value reflects a higher concentration of single layers. The sample with R = 1 indicates the presence of only single-graphene layers and the absence of π -stacked graphene sheets [18,19]. Such a sample can be discerned from the XRD spectrum with (100) yet without (002) peak. In the present case, AAC exhibits a relatively lower *R* value compared with AC. This suggests an enhanced concentration of single layers in AAC, a situation that is beneficial for AAC with enhanced electrochemical performance [18].



Figure 2. Raman spectra of the samples.

To reveal further structural information of AC and AAC, Raman spectra were collected as shown in Fig. 2. The broad peaks centered around 1336 and 1588 cm⁻¹ correspond separately to the D and G Raman bands of activated carbons [11,12,20]. The D band originates from a double resonant Raman process that involves elastic scattering from defects together with one-phonon inelastic scattering, rendering it the characteristic feature for identification of structural disorder and defects in graphitic materials [21]. The G band is related to in-plane vibration of the graphite lattice [11]. As documented in literature [11,12,20,21], the intensity ratio of D to G (I_D/I_G) is considered as a measure of the degree of graphitization for carbon materials. In the present case, the I_D/I_G ratio is decreased to 0.75 for AAC from that of 0.87 for AC (Fig. 2, inset), indicating an enhanced degree of graphitization of AAC [21]. It should be pointed out that this result is contrary to the results in previous reports for activated carbons treated with strong oxidants such as $KMnO_4/(NH_4)_2S_2O_8$ plus H_2SO_4/HNO_3 [11,12] yet in accordance with the results for carbon materials treated with diluted HNO_3 [20,21]. This phenomenon can be rationalized by partial removal of amorphous carbon or even consumption of the most disordered carbon during hydrothermal oxidation [21]. This explanation is in concert with the 11% weight loss of AC after hydrothermal oxidation as mentioned before and supported by the enhanced electric conductivity of AAC compared with that of AC (Table 1). The decrease in I_D/I_G for AAC is accompanied by the narrowing of full width at half-maximum (FWHM) compared with AC (Fig. 2, inset), in accordance with the previous report [21].





Figure 3. (a) FT-IR spectra; (b) XPS survey spectra; (c) C 1s core-level spectra; and (d) O 1s core-level spectra of the samples.

Fig. 3a shows the FT-IR spectra of the samples. Apart from the peaks at 3400, 1575, 1430, 1153, and 886 cm⁻¹ in AC spectrum, a new peak occurs at 1700 cm⁻¹ in AAC spectrum. The former five peaks correspond to the v(O-H) stretching vibration, $v_{as}(C=C)$ stretching vibration, $v_s(C=C)$ stretching vibration, v(C-O) stretching vibration, and $\delta(C_{Ar}-H)/\gamma(O-H)$ deforming vibrations in sequence [12,22,23]. The latter peak is attributed to the v(C=O) stretching vibration of quinone [22]. It should be pointed out the intensity ratio of $v(C-O)/v_{as}(C=C)$ is increased after chemical oxidation. The occurrence of v(C=O) and the increase in intensity ratio of $v(C-O)/v_{as}(C=C)$ indicate that abundant oxygen-containing groups have been formed upon AAC due to chemical oxidation.

To reveal further information on the surface chemistry of the samples, XPS spectra were collected as shown in Fig. 3b–d. The survey spectra (Fig. 3b) exhibit C, O, and trace amount of Si, which arises from inorganic impurities. Apart from Si, other inorganic impurities such as Al, Mg, and Zn can also be detected from the energy dispersive spectrum of AC (Fig. 4a). Through spectral deconvolutions, the core-level spectra of C 1s can be fitted into three peaks centered at 284.8, 285.1, and 286.1/287.3 eV (Fig. 3c and inset), corresponding separately to the C=C, C–OC/C–OH, and C=O components [11,12,24]. Likewise, three peaks centered at 531.5/531.7, 533.5/533.7, 535.1/535.6 eV can be resolved form the O 1s core-level spectra (Fig. 3d and inset), corresponding to the components of C=O, C–O, and surface adsorbed O_2/H_2O in sequence [12].

It should be pointed out there is no peak corresponding to the O–C=O component with binding energy over 288.5 eV in the C 1s spectrum of AAC, different from the result for surface-modified activated carbons in previous reports [11,12,24]. This is because the AAC presented here is obtained from a relatively mild oxidation environment (7.2 mol L⁻¹ HNO₃) while the surface-modified AC in literature are obtained from relatively strong oxidation environments involving O₃ [24] or strong oxidants (e.g. KMnO₄, (NH₄)₂S₂O₈) plus H₂SO₄/HNO₃ [11,12]. Also, the total concentration of the components related to C=O and C–O is increased by 20% for AAC compared with AC. The increase in concentration of C=O/C–O components and the nondetectable O–C=O component facilitate to improve the pseudocapacitance and cycling stability of AAC when used as an electrode material for supercapacitors.



Figure 4. (a) Energy dispersive spectrum of AC; (b) O mapping image corresponding to c; (c) SEM image of AAC; (d) SEM image of AC.

Different from the result that the weight of activated carbon fibers is increased after chemical oxidation in solution [25], the weight of AAC is reduced by 11% in comparison with that of AC, as mentioned before. The weight loss is attributed to the elimination of inorganic impurities by acid erosion.



Figure 5. (a) Nitrogen sorption isotherms; (b) PSD plots; inset in b highlights the PSD of micropores.

The inorganic impurities are confirmed by the energy dispersive spectrum of AC (Fig. 4a), where Al, Mg, Si, and Zn-containing impurities are present. After chemical oxidation in 7.2 mol L^{-1} HNO₃ at 80 °C for 6 h, the weight percent of the inorganic impurities is decreased to be 0.95% from

4.06%, leaving Al, Si, and Zn-containing impurities in AAC. Also, the oxygen mapping image exhibits an uniform distribution of the oxygen species upon AAC (Fig. 4b), a situation that is beneficial for the surface reaction-driven charge storage for supercapacitors [6,12]. Although the composition and the surface of AC can be modified by chemical oxidation, there is no apparent discrepancy in morphology between AC and AAC, both of which are composed of microparticles with micro- and nanostructure (Fig. 4c,d). The size of spherical nanospheres adhered on the microparticles lies in the range of 10–30 nm.

sample	$\frac{S_{\rm BET}}{(\rm m^2~g^{-1})}$	$V_{\text{total pore}}$ (cm ³ g ⁻¹)	$V_{\text{micropore}}$ (cm ³ g ⁻¹)	$\frac{S_{\rm micro}}{({\rm m}^2~{\rm g}^{-1})}$	S _{micro} /S _{BET} (%)	average pore width* (nm)	conductivity (S cm ⁻¹)
AC	1047.3	0.57	0.184	461.4	44.1	5.18	3.3×10^{-5}
AAC	942.4	0.56	0.150	369.3	39.2	5.15	8.5×10^{-5}

Table 1. Physicochemical parameters of the samples.

* BJH adsorption average pore width

3.2. Textural properties

The influence of chemical oxidation on the textural properties of AC is evaluated by collecting the nitrogen sorption isotherms, as shown in Fig. 5a. Both AC and AAC are featured with a micro- and mesoporous characteristic. The micropores are reflected by the dramatic increase in nitrogen adsorption capacity at a lower P/P° range of 0–0.1 [22]. The mesopores are reflected by the type-H4 hysteresis loops at a relatively high P/P° range of 0.5–1 [23]. The coexistence of micropores and mesopores is confirmed by the PSD plots (Fig. 5b and inset), where the pores are concentrated at 0.5–14 nm. As documented in literature, mesopores facilitate to improve the rate capability [26] while micropores especially subnanopores with diameter of 0.7–0.8 nm contribute to anomalous increase in specific capacitance of the electrode materials [27].

The textural parameters of the samples are listed in Table 1. It is found that the values of S_{BET} and parameters related to the pores are decreased for AAC in comparison with those for AC, in accordance with the results in previous reports [22,23,25]. This is attributed to the collapse of some pore walls and/or partial blockage of the micropore entrance by oxygen-containing functional groups introduced by the oxidation treatment [22,23]. Nevertheless, the decrease in S_{BET} in the present case is not as significant as that in previous reports using KMnO₄/(NH₄)₂S₂O₈ plus H₂SO₄/HNO₃ for oxidation of AC [11,12]. This result counterevidences a mild oxidation environment experienced in this research, in concert with the result derived from the C 1s spectra (Fig. 3c).

On the basis of the above analysis, surface-modified AAC has been prepared through chemical oxidation in a mild oxidation environment. The as-obtained AAC is featured with enhanced concentration of single-graphene layers, a micro- and mesoporous characteristic, and surface wealthy in C=O/C-O yet scarce of O-C=O groups, presenting a promising candidate in the role of electrode materials for supercapacitors with enhanced electrochemical performance.

3.3. Electrochemical performance

The CV curves of AC as a function of the scan rates exhibit a quasirectangular shape (Fig. 6a), indicating a typical capacitive behavior due to the simultaneous electrochemical double layer capacitance (EDLC) and pseudocapacitance [28]. The contribution of pseudocapacitance with respect to AC is due to the faradic redox between the electrolyte ions and the oxygen-containing functional groups, which are created during the activation process of carbon materials in concert with the FT-IR result (Fig. 3a). In the case of AAC, the contribution of pseudocapacitance is well reflected by the anodic/cathodic peak pairs (Fig. 6b). The linear relationship between peak currents and scan rates ranging from 1 to 50 mV s⁻¹ indicates the faradaic redox regarding pseudocapacitance is confined to the surface and not diffusion limited (Fig. 6c) [6].



Figure 6. (a) CV curves of AC; (b) CV curves of AAC; (c) plots of peak currents *vs.* scan rates; (d) GCD curves of AC; (e) GCD curves of AAC; (f) plots of $C_g vs.$ current density.

A noteworthy point is that the working potential window for AAC electrode (1.1 V, Fig. 6b) is enlarged by 0.15 V compared with that for AC (0.95 V, Fig. 6a). This is helpful to improve the specific energy of AAC according to the equation of $E = 0.5C\Delta U^2$ [14], where C is the specific capacitance (F g⁻¹), and ΔU the potential window (V).

The GCD curves of AC exhibit a symmetric shape (Fig. 6d), indicating a good capacitive behavior dominated by EDLC. However, the GCD curves of AAC (Fig. 6e) exhibit a nearly symmetric shape with charge/discharge plateaus corresponding to the anodic/cathodic peaks in CV curves (Fig. 6b). The values of gravimetric capacitance (C_g) are evaluated from their discharge curves. Fig. 6f shows the plots of C_g vs. current density. It is apparent that AAC exhibits enhanced C_g values compared with AC in the case of current density smaller than 10 A g⁻¹. For example, the C_g of AAC at 1 A g⁻¹ is 151 F g⁻¹, higher by 33.5 F g⁻¹ than that of AC at the same current density. As the current density increases to over 15 A g⁻¹, the C_g values of AAC are lower than those of AC.



Figure 7. (a) Cycling performance; (b) Nyquist plots.

The enhanced C_g for AAC at relatively low current densities is attributed to the increased concentration of oxygen-containing functional groups, enhanced electric conductivity, and improved concentration of single-graphene layers, as revealed by the XRD, Raman, FT-IR, and XPS spectra (Figs. 1–3). The decrease in C_g for AAC as the current density increases is attributed to the increase in electrode polarization, which is reflected by the increased distance between the anodic and cathodic peaks as the scan rate increases (Fig. 6b). This result indicates that surface modification of activated carbons through chemical oxidation improves the specific capacitance at relatively low current densities but decreases their rate capability.

To put the samples into practical applications, their cycling performance was evaluated through a three-electrode mode, as shown in Fig. 7a. Although the capacity retention of AC (97.3%) is higher than that of AAC (83.9%) after 5000 cycles, the retained C_g of the latter (126.7 F g⁻¹) is higher than that of the former (113.7 F g⁻¹). Also, the Coulombic efficiency for AC and AAC during the cycling is close to 100%, respectively. The superior cycling performance of AAC is attributed to the reversible redox between the electrolyte ions and the C=O/C–O sites, as expressed by eq (2):

The decrease in specific capacitance during the cycling is attributed to the irreversible reaction involving decomposition of carboxyl groups (eq (3)), which mainly arise from the electrochemical oxidation of C=O/C–O during the charge process [6]. Certainly, we cannot exclude the negative contribution from the trace amount of carboxyls produced by chemical oxidation during sample preparation, although they have not been resolved from the C 1s spectrum (Fig. 3c).

The difference in electrochemical performance between AC and AAC can be reflected by their Nyquist plots (Fig. 7b). At the high frequency region, the equivalent series resistances (ESRs) of AC and AAC are measured to be 0.51 and 0.66 Ω , respectively. There are no semicircles at frequencies higher than that of the onset of the diffusion limited response, i.e. the 45° sloping lines in the Nyquist plots. This is attributed to that the charge/discharge rates are merely limited by the electrode capacitance and resistance rather than by the kinetics of the electrode reactions [29]. At the low frequency region, the plot of AAC approaches much nearer to the imaginary axis compared with that of AC, indicating a more ideal capacitive response of the former [29]. In addition, there is no distinct change in ESRs for AC and AAC, respectively, before and after 5000 cycles. This result indicates a good structural stability of AC and AAC. However, the plots deviate from the imaginary axis after 5000 cycles, indicating a reduced capacitive response of the electrode materials.

4. CONCLUSION

In summary, AAC with surface carrying oxygen functional groups has been prepared through chemical oxidation in nitric acid solution. The samples are characterized with XRD, Raman, FT-IR, XPS, SEM, mapping, and S_{BET} techniques, and further tested in the role of electrode materials for supercapacitors. The scientific significance of this research lies in: (1) surface modification of AC in a mild oxidation environment offers AAC with surface wealthy in C=O and C–O yet scarce of O–C=O groups; (2) the working potential window of AAC is enlarged by 0.15 V compared with that of AC, a situation that is beneficial for improvement of the specific energy; and (3) the oxygen-containing functional groups make positive contribution to the specific capacitance of AAC at current densities lower than 10 A g⁻¹ but negative contribution to the rate capability and cycling stability as the current density increases to over 15 A g⁻¹, providing useful information on improving the electrochemical performance of carboneous materials through solution-based chemical oxidation.

ACKNOWLEDGMENTS

This research is financially supported by National Natural Science Foundation of China under Grant No. 51272143.

References

- 1. L. Cermakova, I. Kopecka, M. Pivokonsky, L. Pivokonska and V. Janda, *Sep. Purif. Technol.*, 173 (2017) 330.
- 2. M.B. Joseph, A. Colburn, T.P. Mollart, N. Palmer, M.E. Newton and J.V. Macpherson, *Sens. Actuators B*, 238 (2017) 1128.
- 3. K. Qi, R. Selvaraj, T.A. Fahdi, S. Al-Kindy, Y. Kim, G.C. Wang, C.W. Tai and M. Sillanpää, *Appl. Surf. Sci.*, 387 (2016) 750.
- 4. Y. Wang, W. Shi, S. Wang, C. Li, M. Qian, J. Chen and R. Huang, Carbon, 108 (2016) 146.
- 5. H. Yuan, Q. Jiao, S. Zhang, Y. Zhao, Q. Wu and H. Li, J. Power Sources, 325 (2016) 417.
- 6. Y. Shao, J. Xiao, W. Wang, M. Engelhard, X. Chen, Z. Nie, M. Gu, L. V. Saraf, G. Exarhos, J. G. Zhang and J. Liu, *Nano Lett.*, 13 (2013) 3909.
- W.K. Chee, H.N. Lim, Z. Zainal, N.M. Huang, I. Harrison and Y. Andou, J. Phys. Chem. C, 120 (2016) 4153.
- 8. G. Sethia and A. Sayari, Carbon, 99 (2016) 289.
- X. Yue, W. Sun, J. Zhang, F. Wang, Y. Yang, C. Lu, Z. Wang, D. Rooney and K. Sun, J. Power Sources, 331 (2016) 10.
- 10. S.Y. Kim and B.H. Kim, J. Power Sources, 328 (2016) 219.
- 11. S. Gao, L. Zhu, L. Liiu, A. Gao, F. Liao and M. Shao, Electrochimica Acta, 191 (2016) 908.
- 12. C. Liu, B.B. Koyyalamudi, L. Li, S. Emani, C. Wang and L.L. Shaw, Carbon, 109 (2016) 163.
- 13. D. Qu, J. Power Sources, 109 (2002) 403.
- 14. J. Zhou, J. Lian, L. Hou, J. Zhang, H. Gou, M. Xia, Y. Zhao, T.A. Strobel, L. Tao and F. Gao, *Nat. Commun.*, 6 (2015) 8503.
- 15. G. Lota, J. Tyczkowski, R. Kapica, K. Lota and E. Frackowiak, J. Power Sources, 195 (2010) 7535.
- 16. Y.R. Nian and H. Teng, J. Electrochem. Soc., 149 (2002) A1008.
- 17. S. Wang, L. Gai, J. Zhou, H. Jiang, Y. Sun and H. Zhang, J. Phys. Chem. C, 119 (2015) 3881.
- 18. Y. Liu, J.S. Xue, T. Zheng and J.R. Dahn, Carbon, 34 (1996) 193.
- 19. J. Collins, D. Zheng, T. Ngo, D. Qu and M. Foster, Carbon, 79 (2014) 500.
- 20. J. Collins, T. Ngo, D. Qu and M. Foster, Carbon, 57 (2013) 174.
- 21. V. Likodimos, T.A. Steriotis, S.K. Papageorgiou, G.E. Romanos, R.R.N. Marques, R.P. Rocha, J.L. Faria, M.F.R. Pereira, J.L. Figueiredo, A.M.T. Silva and P. Falaras, *Carbon*, 69 (2014) 311.
- 22. J. Jaramillo, P.M. Álvarez and V. Gómez-Serrano, Fuel Process. Technol., 91 (2010) 1768.
- 23. L. Wu, S. Sitamraju, J. Xiao, B. Liu, Z. Li, M.J. Janik and C. Song, Chem. Eng. J., 242 (2014) 211.
- 24. S.J. Park and B.J. Kim, Mater. Sci. Eng. A, 408 (2005) 269.
- 25. C.L. Mangun, K.R. Benak, M.A. Daley and J. Economy, Chem. Mater., 11 (1999) 3476.
- 26. Z. Wang, D.O. Carlsson, P. Tammela, K. Hua, P. Zhang, L. Nyholm and M. Strømme, *ACS Nano.*, 9 (2015) 7563.
- 27. J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon and P.L. Taberna, *Science*, 313 (2006) 1760.
- 28. S.H. Park, S.B.Yoon, H.K. Kim, J.T. Han, H.W. Park, J. Han, S.M. Yun, H.G. Jeong, K.C. Roh and K.B. Kim, *Sci. Rep.*, 4 (2014) 6118.
- 29. G. Nyström, M. Strømme, M. Sjödin and L. Nyholm, *Electrochimica Acta.*, 70 (2012) 91.

© 2017 The Authors. Published by ESG (<u>www.electrochemsci.org</u>). 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/).