We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Oxidation-Ultrasound Process on Removing Potassium Ions from Activated Carbon for Improving Electrochemical Properties of Supercapacitor

Kang Sun

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/64809>

Abstract

To produce pure activated carbon (AC) with low potassium ions (K^+) content for supercapacitor, coconut-shell AC activated by KOH was treated with a novel oxidation-ultrasound process on the basis of hydrochloric acid (HCl) washing. The electrochemical performances of the ACs as supercapacitor electrodes were characterized by cyclic voltammetry (CV), galvanostatic charge-discharge (GC), and electrochemical impedance spectroscopy (EIS). Results showed that the obtained AC, which was washed with 1.0 wt% HCl solution for 120 min and subsequently treated with 0.6 wt% H_2O_2 solution at 60°C in an ultrasonic oscillator for 8 h, possessed a K^+ content of 46 mg/kg, much lower than that of 417 mg/kg of the AC without oxidation-ultrasound treatment. Furthermore, a large specific surface area and pore volume of 3460 m^2/g and 1.869 cm^3/g , respectively, were obtained for AC after oxidation-ultrasound treatment. A high specific capacitance of 306 F/g at the current density of 1 A/g in 1 M H_2SO_4 electrolyte was observed for the prepared AC, indicating it has good electrochemical performances, and remained at 294 F/g with a capacitance retention of 96% after 3000 cycles, indicating excellent stability and capacitive behavior of the AC electrode for supercapacitor.

Keywords: activated carbon, potassium ions, oxidation-ultrasound, specific capacitance, supercapacitor

1. Introduction

As a kind of new energy storage device between battery and conventional capacitor, supercapacitor has drawn much attention recently due to its high power density and long cycle life [1–4]. Besides, it was assumed to be one of the most promising energy storage devices for

various applications such as brake energy recovery systems, hybrid electrical vehicles, digital telecommunication systems [5, 6], etc. It is known that the surface area, pore size, and purity texture have significant influence on the performances of supercapacitor for the electrode material [7]. So far, AC has been widely applied in electrode material for supercapacitor applications, owing to its advantages of good chemical stability and conductivity, large surface area, low cost [8–11], etc. However, the AC products show a high K^+ content due to the process limitations of KOH activation, as a result, the already-formed AC pores were blocked, which had a negative effect on the specific capacitance and cycle life of supercapacitor. Therefore, it is necessary to remove the K^+ from the AC, aiming to greatly improve the electrochemical performances of supercapacitor.

In general, the K^+ existed in the AC often spreads in the pores, and HCl washing cannot efficiently remove it. Although ultrasound oscillation was effective to disperse K^+ into solution, oxidation process is able to weaken the force between AC pore walls and K^+ , resulting in deeply purification of the AC samples. Therefore, this study aims to make use of a novel oxidation-ultrasound process to reduce the K^+ content of ACs. The effect of K^+ content on AC properties will be reflected by the physical and electrochemical performances.

2. Experimental

2.1. Preparation of AC sample

In this study, coconut shell was used to prepare AC by KOH activation. First of all, the coconut shell was subjected to be carbonized at 600°C for 1 h and was crushed to obtain a particle size of about 1 mm. Then 50 wt% KOH solution with the KOH/C weight ratio of 4:1 was mixed with the coconut shell carbide in a stainless steel reactor. In addition, the mixture was activated in a muffle furnace in which the mixture was first pretreated at 350°C for 2 h under air atmosphere, then heated up to 800°C at a heating rate of 10°C min⁻¹, and maintained at 800°C for 1 h under sealed condition. After cooled down to the room temperature, the resultant samples were subsequently washed with distilled water until a pH of approximately 6 was obtained. Finally, the prepared AC samples were dried at 120°C for 10 h under vacuum condition.

2.2. Removal of the K^+ from AC sample

There are two steps included in the removal process of the K^+ . In the first step, 2.0 g as-obtained AC was impregnated with 100 ml 0.3, 0.5, 0.7, 1.0, and 1.2 wt% of HCl solution, respectively. Then the mixture was stirred at 80°C for 30–150 min in an electro-thermostatic water cabinet. The oxidation-ultrasound process was used to purify the HCl-washed AC deeply in the second step. In an ultrasonic oscillator, 100 ml different weight ratios 0, 0.2, 0.4, 0.6, 0.8, and 1.0 wt% of H₂O₂ solution were mixed with 2.0 g HCl-washed AC for 2–10 h at 10–80°C. The final treated samples were dried at 120°C under vacuum condition overnight. After that, the resulting AC samples were named AC-W, AC-W-H, and AC-W-H-U, corresponding to the water, HCl, and oxidation-ultrasound treatment on AC, respectively.

2.3. Characterizations

Inductively coupled plasma mass spectrometry (ICP-MS) was used to measure the K^+ content of ACs. Scanning electron microscopy (SEM, S-3400, Hitachi) was used to exhibit the surface morphologies of the samples. Nitrogen (77 K) adsorption was carried out using a Micromeritics ASAP 2020 analyzer to detect the porous properties of ACs. The specific surface area values, total pore volume, and the pore size distribution of activated carbons were calculated by the BET method, according to the adsorbed amount and density functional theory (DFT), respectively.

2.4. Electrochemical characterization

The capacitive performance measurements were carried out at room temperature in a three-electrode system on an electrochemical workstation (Bio-Logic, France) in 1 M H_2SO_4 electrolyte. The active AC materials, acetylene black, and 5 wt% PTFE with a weight ratio of 8.5:1:0.5 were fully mixed and grounded in a mortar. Then the mixture was pressed onto a Ni-foam current collector to form the working electrode. And Ag/AgCl and platinum foil were employed as the reference and counter electrode, respectively. The capacitive behavior of the AC electrode was characterized by CV, GCD, and electrochemical impedance spectroscopy (EIS) measurements. CV was performed from 0.01 to 0.9 V at various scan rates in a range of 5–200 $mV s^{-1}$, GC curve was measured from 0.01 to 0.9 V at different current densities ranging from 0.1 to 5 Ag^{-1} , and EIS was recorded at the frequency from 100 kHz to 10 MHz.

3. Results and discussion

3.1. Influencing factors on removal process of K^+

3.1.1. Effect of HCl treatment on the K^+ content of AC

In this paper, HCl solution is first used to treat with the AC-W samples to remove the K^+ . The effects of the treatment time and mass fraction of HCl solution are investigated in detail. It can be seen in **Figure 1(a)** that the relationship between the mass fraction of HCl solution and K^+ content for 90 min. And the figure also shows the K^+ content exhibits a conspicuous decrease with the increasing mass fraction of HCl solution from 0 to 1.0 wt%, and then it presents a rising trend. The excessive acid radical ions results in K^+ removed from AC difficulty during electric double layer process, which is formed on the surface of K^+ . Thus, the optimal mass fraction of HCl solution is 1.0 wt%.

It shows the relationship between K^+ content and the treatment time of HCl solution at the mass fraction of 1.0 wt% in **Figure 1(b)**. The content of K^+ decreases from 1242 to 417 mg/kg significantly, while the treatment time increases from 30 min to 2 h, and it does not change anymore after 2 h. Therefore, treatment time of 120 min and 1.0 wt% HCl solution are chosen as the optimal treatment conditions for the whole experiments, and the corresponding AC sample is named AC-W- $H_{1\%/120min}$.

Figure 1. Effect of mass fraction and treatment time of HCl solution on the K⁺ content of AC.

3.1.2. Effect of oxidation-ultrasound process on the K⁺ content of AC

The AC-W-H_{1%/120min} is then subjected to oxidation-ultrasound process to deeply remove the K⁺. The influence of the mass fraction of H₂O₂ solution, ultrasound temperature, and ultrasound time on the K⁺ content of ACs is studied. The obtained results are shown in **Table 1** and **Figure 2**. The mass fraction of H₂O₂ solution is in the range of 0–1.0 wt% at an ultrasound time of 6 h and an ultrasound temperature of 60°C. **Table 1** indicates that the K⁺ content of AC without H₂O₂ treatment is 256 mg/kg, substantially lower than that of the AC-W-H_{1%/120min} with 417 mg/kg, which should have close relationships with the ultrasonic effect that the ultrasonic wave can accelerate the mass transfer process of them between the solid-liquid phase and promote some uncarbonized substances inside the AC pores to be dispersed into the solution along with the K⁺. It can be seen from **Figure 2(a)** that the K⁺ content of AC decreases markedly from 256 to 61 mg/kg, and thereafter it remains substantially unchanged when the mass fraction of H₂O₂ solution increased from 0 to 0.6 wt%. Therefore, it can be stated that H₂O₂ treatment shows a great effect on producing ACs with low K⁺ content. On the one hand, as an oxidizing agent, H₂O₂ solution can reduce the force between the K⁺ and AC pore walls, leading to it transferred to the solution easily. On the other hand, the K⁺ in the AC can coexist with some organic groups in the form of chemical bond, which can be destroyed by the presence of H₂O₂ solution, making it possible for the K⁺ of ACs to be removed effectively [12, 13].

Mass fraction of H ₂ O ₂ /wt%	0	0.2	0.4	0.6	0.8	1.0
K ⁺ content/(mg/kg)	256	184	92	61	64	75
Ultrasonic temperature/°C	10	20	40	60	70	80
K ⁺ content/(mg/kg)	157	124	96	61	74	91
Ultrasonic time/h	2	4	6	8	10	12
K ⁺ content/(mg/kg)	148	119	61	46	41	44

Table 1. Results of mass fraction of H₂O₂ solution, ultrasound temperature and ultrasound time on the K⁺ content of AC.

Figure 2. Effect of mass fraction of (a) H₂O₂ solution, (b) ultrasound temperature and (c) ultrasound time on the K⁺ content of AC.

Figure 2(b) exhibits the relationship between K⁺ content and the ultrasound temperature in the range of 10~80°C at an ultrasound time of 6 h, using 0.6 wt% H₂O₂ solution. It was observed that the K⁺ content of AC decreased from 157 to 61 mg/kg when the temperature increased from 10 to 60°C, but increased while the temperature was further increased from 60 to 80°C. This might be attributed to the fact that the energy and activity of the K⁺ were improved with the increase of temperature in ultrasonic field and the movement of K⁺ into the solution was accelerated. **Figure 2(c)** shows the effect of ultrasound time on the K⁺ content of AC, using 0.6 wt% H₂O₂ solution at the ultrasound temperature of 60°C. It is clear that the K⁺ content drops from 148 to 46 mg/kg as the ultrasound time increases from 2 to 8 h, and it scarcely changes with a continuing increase of ultrasound time. Therefore, we consider 0.6 wt% H₂O₂ solution, ultrasound temperature of 60°C and ultrasound time of 8 h as the optimum experiment conditions to deeply remove the K⁺ from AC, and the corresponding AC is marked as AC-W-H_{1%/120min}-U_{0.6%/60°C/8h}.

3.2. Sample characterization

3.2.1. Morphology characterization

Figure 3(a–c) shows the surface morphologies of the AC-W, AC-W-H_{1%/120min} and AC-W-H_{1%/120min}-U_{0.6%/60°C/8h} by SEM at 1000× magnification. It can be seen clearly that the morphologies of the AC samples display an obvious change on the surface. The AC-W has large quantities of uncarbonized substances presented on the surface. The AC-W-H_{1%/120min} has relatively flat and smooth surface compared to the AC-W, but there are still some residues on the surface. Meanwhile, as shown in **Figure 3(c)**, the surface of the AC-W-H_{1%/120min}-U_{0.6%/60°C/8h} was very clean and smooth, confirming that the oxidation-ultrasound process has a significant effect on the purification of AC, which is consistent with the aforementioned results of the K⁺ content.

Figure 3. SEM images of (a) AC-W, (b) AC-W-H_{1%/120min} and (c) AC-W-H_{1%/120min}-U_{0.6%/60°C/8h}.

3.2.2. Porous texture characterization

It was reported that the specific surface area and pore size of AC were critical factors for electrochemical capacitor applications [14], hence, the N₂ adsorption-desorption isotherms and corresponding pore size distribution curves of the as-prepared ACs were analyzed as shown in **Figure 4**. **Table 2** gives the textural characteristics and specific capacitance of the samples. It was noticed that the presented isotherms were type I for all samples according to IUPAC

classification [15, 16]. The N_2 adsorption volume of the AC-W achieved saturation at low relative pressure of 0.1 and the lowest isotherm was observed, suggesting that a great number of activating agents (KOH) are still blocking in the AC pores, especially the mesopores. The AC-W- $H_{1\%/120min}$ displays significantly higher isotherm than the AC-W and its N_2 adsorption volume shows a gradual increase until the relative pressure of 0.4, implying that most of the KOH remained in the AC pores are removed by HCl washing. As for the AC-W- $H_{1\%/120min}$ - $U_{0.6\%/60^\circ C/8h}$. The existence of a hysteresis loop in the desorption branch at the relative pressure of 0.47 was observed obviously. And the isotherm with a highest adsorbed volume indicated that the deep removal of the K^+ along with other residues from the AC pores by the oxidation-ultrasound process greatly increased the mesopore volumes.

Figure 4. (a) N_2 adsorption-desorption isotherms and (b) the corresponding pore size distributions of the as-prepared samples.

Samples	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{meso} (cm^3/g)	V_{micro} (cm^3/g)	D_p (nm)	C_g (F/g)	Ash (wt.%)	Yield (%)
AC-W	2198	1.110	0.311	0.799	1.781	147	1.2	—
AC-W- $\text{H}_{1\%/120\text{min}}$	3178	1.686	1.297	0.389	2.086	255	0.1	94.3
AC-W- $\text{H}_{1\%/120\text{min}}-\text{U}_{0.6\%/60^\circ\text{C}/8\text{h}}$	3460	1.869	1.615	0.254	2.228	306	0.01	97.5

Note: S_{BET} : specific surface area; V_t : total pore volume; V_{meso} : mesopore volume; V_{micro} : micropore volume; D_p : average pore size; C_g : specific gravimetric capacitance; yield: the independent result of every step for removing K^+ .

Table 2. Textural characteristics and specific capacitance of the as-prepared samples.

Figure 4(b) gives the pore size distributions of the as-prepared ACs. Results showed that the pore size of AC-W was in the range of 0.6–2 nm, while that of AC-W- $\text{H}_{1\%/120\text{min}}-\text{U}_{0.6\%/60^\circ\text{C}/8\text{h}}$ and AC-W- $\text{H}_{1\%/120\text{min}}$ ranged from 2 to 4 nm and 0.5 to 2.0 nm, respectively. It is obvious that the purification of the AC-W with HCl and oxidation-ultrasound treatment in turn gradually made mesopores (2–4 nm) become the dominant type of pores.

It can be seen from **Table 2** that the AC-W had an average pore size of 1.781 nm a mesopore volume of $0.311 \text{ cm}^3/\text{g}$, while the AC-W- $\text{H}_{1\%/120\text{min}}$ and AC-W- $\text{H}_{1\%/120\text{min}}-\text{U}_{0.6\%/60^\circ\text{C}/8\text{h}}$ achieve the mesopore volume of 1.297 and $1.615 \text{ cm}^3/\text{g}$, and the average pore size of 2.086 and 2.228 nm, respectively. Moreover, the AC-W- $\text{H}_{1\%/120\text{min}}$ has significantly larger surface area and total pore volume than the AC-W, increasing respectively from 2198 to $3178 \text{ m}^2/\text{g}$ and 1.110 to $1.686 \text{ cm}^3/\text{g}$, and the AC-W- $\text{H}_{1\%/120\text{min}}-\text{U}_{0.6\%/60^\circ\text{C}/8\text{h}}$ possesses the largest surface area and pore volume of $3460 \text{ m}^2/\text{g}$ and $1.869 \text{ cm}^3/\text{g}$. It is evident that the removal of K^+ from AC samples creates some new microspores and obviously promotes the widening of existing micropores into mesopores at the same time, which can be accessible to electrolyte ions for electrical double-layer formation [17]. Thus, the large surface area, high pore volume, and low K^+ content of AC samples make them good candidates for electrode materials.

3.3. Electrochemical characterization

CV is used in determination of the electrochemical performances of as-prepared samples. The typical CV results of AC-W, AC-W- $\text{H}_{1\%/120\text{min}}$ and AC-W- $\text{H}_{1\%/120\text{min}}-\text{U}_{0.6\%/60^\circ\text{C}/8\text{h}}$ at the scan rate of 10 mV/s with the potential range of $-0.2\sim 0.8 \text{ V}$ are shown in **Figure 5(a)**. Results showed that all the AC electrodes displayed an approximately quasi-rectangular voltammogram shape, which was the characteristic of electrochemical double-layer capacitance [18–20]. Furthermore, the CV curve of AC-W- $\text{H}_{1\%/120\text{min}}-\text{U}_{0.6\%/60^\circ\text{C}/8\text{h}}$ electrode exhibits a bigger current response and larger area of rectangle than that of the AC-W and AC-W- $\text{H}_{1\%/120\text{min}}$ electrode, demonstrating an obvious increase in capacity during the removal process of K^+ . **Figure 5(b)** shows the CV curves of the AC-W- $\text{H}_{1\%/120\text{min}}-\text{U}_{0.6\%/60^\circ\text{C}/8\text{h}}$ electrode at different scan rates of 5–50 mV/s. The CV curve eventually becomes titled with the increase of the scan rate, but still maintains a rectangular-like shape even at 50 mV/s, implying a small resistance in the accessible pores and an excellent capacitive behavior [21, 22] of the AC-W- $\text{H}_{1\%/120\text{min}}-\text{U}_{0.6\%/60^\circ\text{C}/8\text{h}}$ electrode.

Figure 5. Cyclic voltammograms of the samples: (a) all AC electrodes at a scan rate of 10 mV/s and (b) AC-W-H_{1%/120min}-U_{0.6%/60°C/8h} with different scan rates.

GC measurements have also been conducted to investigate the electrochemical performances of as-prepared samples. **Figure 6(a)** shows the GC curves of the AC-W, AC-W-H_{1%/120min} and AC-W-H_{1%/120min}-U_{0.6%/60°C/8h} at the current density of 1 A/g with the potential range of -0.2–0.8 V. It can be seen that all the samples present a virtually linear shape and isosceles triangle curve, indicating a good reversibility and typically capacitive behavior of the AC electrodes [23, 24]. According to the GC curves, the AC-W-H_{1%/120min}-U_{0.6%/60°C/8h} has longer discharging time compared to the AC-W and AC-W-H_{1%/120min}, implying larger specific capacitance, which proved that the deep removal of K⁺ from AC samples had a significant effect on the electrochemical performance of AC electrode.

Figure 6. Galvanostatic charge/discharge curves of the samples: (a) all activated carbon electrodes at a current density of 1 A/g and (b) AC-W-H_{1%/120min}-U_{0.6%/60°C/8h} with different current densities.

Figure 6(b) represents the GC curves of the AC-W-H_{1%/120min}-U_{0.6%/60°C/8h} measured in a current density range of 0.5–5 A/g. It was obvious that the discharging time dropped as the current density increased, while the curve was constant as typical triangle shape even at a high loading current density of 5 A/g, revealing that the AC-W-H_{1%/120min}-U_{0.6%/60°C/8h} as electrode material is promising for a high performance supercapacitor. In addition, the specific capacitance of the AC electrodes can be calculated from the charge-discharge curves based on the following equation [25, 26]:

$$C_g = 2 \frac{I \cdot \Delta t}{m \cdot \Delta V} \quad (1)$$

where C_g is the specific gravimetric capacitance (F/g), I is the current loaded, Δt is the discharge time (s), ΔV is the potential change during the discharge process, and m (g) represents the mass of the AC. As shown in **Table 2**, the AC-W-H_{1%/120min}-U_{0.6%/60°C/8h} has the highest specific gravimetric capacitance of 306 F/g, which is more than twice as large as that of the AC-W (147 F/g), and increases by about 20% compared with the AC-W-H_{1%/120min} (255 F/g). The enhanced specific capacitance of AC samples can be ascribed to the enhancement of the surface area, effective pore volume and purity, as confirmed by the above results of K⁺ content and N₂ adsorption-desorption isotherms.

Figure 7. Cyclic performances of the samples at a current density of 1 A/g.

Figure 7 shows the cyclic stability of AC-W, AC-W-H_{1%/120min} and AC-W-H_{1%/120min}-U_{0.6%/60°C/8h} electrodes detected by galvanostatic charge-discharge at the current density of 1 A/g for 3000 cycles. The specific capacitance of AC-W decreased obviously from 147 to 125 F/g after 1000 cycles and was maintained at about 116 F/g with the capacitance retention of 79% after 3000 cycles. The specific capacitance of AC-W-H_{1%/120min} is relatively stable and achieves capacitance retention of 91% after 3000 cycles. The specific capacitance for AC-W-H_{1%/120min}-U_{0.6%/60°C/8h} is found to be 306 F/g in the first cycle and 294 F/g after 3000 cycles with a coulombic efficiency of 96%, revealing the excellent stability and reversibility of the AC-W-H_{1%/120min}-U_{0.6%/60°C/8h} electrode.

Figure 8. Nyquist plots of the as-prepared samples (inset: enlarged high-frequency region of Nyquist plots).

EIS measurements are employed to obtain impedance performance information. Typical Nyquist plots for AC-W, AC-W-H_{1%/120min} and AC-W-H_{1%/120min}-U_{0.6%/60°C/8h} electrodes are presented in **Figure 8**. Results revealed that a semicircle in the high-frequency region and a straight line in the low-frequency region were observed in all the three plots [27]. And the plot of AC-W-H_{1%/120min}-U_{0.6%/60°C/8h} sample displays a relatively smaller semicircle than that of AC-W and AC-W-H_{1%/120min} samples in the high-frequency region, indicating a lower charge transfer resistance. This may be ascribed to the larger mesopore volume and lower K⁺ content of AC-W-H_{1%/120min}-U_{0.6%/60°C/8h}, which can facilitate the rapid diffusion of electrolyte ions into the pores of electrode materials. In addition, the AC-W-H_{1%/120min}-U_{0.6%/60°C/8h} shows more vertical line leaning to imaginary axis in the low-frequency region [28], suggesting better capacitive behavior than AC-W and AC-W-H_{1%/120min}.

4. Conclusions

In this work, ACs with high performance for supercapacitor are prepared from coconut shell by KOH activation, using a novel oxidation-ultrasound process to deeply remove the K⁺ of AC. The experiment results demonstrate that the AC samples washed with 1.0 wt% HCl solution for 120 min and subsequently treated with 0.6 wt% H₂O₂ solution at 60°C in an ultrasonic oscillator for 8 h possess a very low K⁺ content of 46 mg/kg. Compared to the AC-W and AC-W-H_{1%/120min}, the AC-W-H_{1%/120min}-U_{0.6%/60°C/8h} exhibits a larger surface area and pore volume of 3460 m²/g and 1.869 cm³/g. As the electrode material for electrochemical application, the AC-W-H_{1%/120min}-U_{0.6%/60°C/8h} showed a high specific capacitance of 306 F/g with a coulombic efficiency of 96% after 3000 cycles. The oxidation-ultrasound process has a great potential to produce ACs with high performance for supercapacitor applications.

Acknowledgements

This research is financially supported by the projects in Forestry Public Benefit Research Sector (Grant No. 201404610) and the National Natural Science Foundation of China (Grant No. 31400510).

Author details

Kang Sun

Address all correspondence to: sunkang0226@163.com

Institute of Chemical Industry of Forest Products, CAF, Nanjing, China

References

- [1] X.J. He, Y.J. Geng, J.S. Qiu, M.D. Zheng, S. Long and X.Y. Zhang, *Carbon*, 2010, 48, 1662-1669.
- [2] B.E. Conway, *Electrochemical supercapacitors. Scientific fundamentals and technological applications*. Kluwer Academic Plenum Press, New York, 1999.
- [3] X.L. Li, C.L. Han, X.Y. Chen and C.W. Shi, *Microporous and Mesoporous Materials*, 2010, 131, 303-309.
- [4] T.E. Rufford, D. Hulicova-Jurcakova, K. Khosla, Z.H. Zhu and G.Q. Lu, *Journal of Power Sources*, 2010, 195, 912-918.
- [5] H. Gómez, M.K. Ram, F. Alvi, P. Villalba, E.L. Stefanakos and A. Kumar, *Journal of Power Sources*, 2011, 196, 4102-4108.
- [6] C.S. Yang, Y.S. Jang and H.K. Jeong, *Current Applied Physics*, 2014, 14, 1616-1620.
- [7] F. Gao, G.H. Shao, J.Y. Qu, S.Y. Lv, Y.Q. Li and M.B. Wu, *Electrochimica Acta*, 2015, 155, 201-208.
- [8] S. Kumagai, M. Sato and D. Tashima, *Electrochimica Acta*, 2013, 114, 617-626.
- [9] T. Zhang, M.B. Zheng, N.W. Li, H.L. Lu, S.T. Zhang and J.M. Cao, *Materials Letters*, 2013, 105, 43-46.
- [10] V. Ruiz, C. Blanco, E. Raymundo-Piñero, V. Khomenko, F. Béguin and R. Santamaría, *Electrochimica Acta*, 2007, 52, 4969-4973.

- [11] H.R. Yu, S. Cho, M.J. Jung and Y.S. Lee, *Microporous and Mesoporous Materials*, 2013, 172, 131-135.
- [12] J.J. Rueda-Márquez, M. Sillanpää, P. Pocostales, A. Acevedo and M.A. Manzano, *Water Research*, 2015, 71, 85-96.
- [13] Y.W. Wang, Y.S. Wei and J.X. Liu, *Journal of Hazardous Materials*, 2009, 169, 680-684.
- [14] Y. Xiao, C. Long, M.T. Zheng, H.W. Dong, B.F. Lei, H.R. Zhang and Y.L. Liu, *Chinese Chemical Letters*, 2014, 25, 865-868.
- [15] X.J. He, P.H. Ling, M.X. Yu, X.T. Wang, X.Y. Zhang and M.D. Zheng, *Electrochimica Acta*, 2013, 105, 635-641.
- [16] S.J. Han, Y.H. Kim, K.S. Kim and S.J. Park, *Current Applied Physics*, 2012, 12, 1039-1044.
- [17] N.D. Kim, W. Kim, J.B. Joo, S. Oh, P. Kim, Y. Kim and J. Yi, *Journal of Power Sources*, 2008, 180, 671-675.
- [18] L. Wei and G. Yushin, *Carbon*, 2011, 49, 4830-4838.
- [19] M.X. Wang, C.Y. Wang, M.M. Chen, Y.S. Wang, Z.Q. Shi, X. Du, T.Q. Li and Z.J. Hu, *New Carbon Materials*, 2010, 25, 285-290.
- [20] X. Du, C.Y. Wang, M.M. Chen, Y. Jiao and J. Wang, *Journal of Physical Chemistry C*, 2009, 113, 2643-2646.
- [21] H.J. Shen, E.H. Liu, X.X. Xiang, Z.Z. Huang, Y.Y. Tian, Y.H. Wu, Z.L. Wu and H. Xie, *Materials Research Bulletin*, 2012, 47, 662-666.
- [22] M.B. Wu, R.C. Li, X.J. He, H.B. Zhang, W.B. Sui and M.H. Tan, *New Carbon Materials*, 2015, 30, 86-91.
- [23] X.X. Xiang, E.H. Liu, Z.Z. Huang, H.J. Shen, Y.Y. Tian, C.Y. Xiao, J.J. Yang and Z.H. Mao, *Journal of Solid State Electrochemistry*, 2011, 15, 2667-2674.
- [24] D.S. Patil, S.A. Pawar, R.S. Devan, Y.R. Ma, W.R. Bae, J.H. Kim and P.S. Patil, *Materials Letters*, 2014, 117, 248-251.
- [25] A. Davies and A. Yu, *Canadian Journal of Chemical Engineering*, 2011, 89, 1342-1357.
- [26] M.B. Wu, P.P. Ai, M.H. Tan, B. Jiang, Y.P. Li, J.T. Zhang, W.T. Wu, Z.T. Li, Q.H. Zhang and X.J. He, *Chemical Engineering Journal*, 2014, 245, 166-172.
- [27] J.L. Chang, Z.Y. Gao, X.R. Wang, D.P. Wu, F. Xu, X. Wang, Y.M. Guo and K. Jiang, *Electrochimica Acta*, 2015, 157, 290-298.
- [28] I. Oh, M. Kim and J. Kim, *Microelectronics Reliability*, 2015, 55, 114-122.