

High Specific Surface Area Rice Hull Based Porous Carbon Prepared for EDLCs

Haibin Chen¹, Haibo Wang¹, Lufeng Yang¹, Yong Xiao², Mingtao Zheng², Yingling Liu^{*2}, Honggang Fu^{*3}

¹Department of Chemistry and Institute of Nanochemistry, Jinan University, Huangpu West Road 601, Guangzhou 510632, PR China

²College of Science, South China Agricultural University, Wushan Lu 483, Guangzhou 510642, PR China

³School of Chemistry and Materials Science, Harbin 150080, PR China

*² E-mail: tliuyl@163.com

*³ E-mail: fuhg@vip.sina.com

Received: 18 April 2012 / Accepted: 11 May 2012 / Published: 1 June 2012

High specific surface area (approximately 4000m²/g) rice hull based porous carbon was carbonized at 400°C for 2 h, followed by alkali hydroxide activation and heating to 800°C. The effects of preparation parameters on the characteristics of these rice hull based porous carbon were studied; the properties of these samples were investigated by BET surface area, X-ray diffraction, CHNS/O Elemental Analyze. The cyclic voltammetry (CV) measurement shows that the synthesized porous carbon exhibited a super capacitance of 368F/g at the scanning rate of 2mv/s.

Keywords: rice hull, porous carbon, high specific surface area, super capacitance

1. INTRODUCTION

Rice hull is an important agriculture residues, it was reported that the world's annual rice production is 5.71 billion tons, in which the rice hull available for using is 1.44 billion tons and the annual yield of China is about 40million tons [1]. However, most of RL (rice hull) is burned as wastes, it not only waste energy but also influences the air quality. So, make use of rice hull is urgent. Recently, porous carbon using rice hull as raw material has attracted great attention for their applications in electric double layer capacitors (EDLC) [2]. EDLC, similar to a conventional capacitor, stores charge electro statically, it has caused attention by virtue of their long cycle life, highly reversible charge storage process, rapid charge-discharge and high specific power density. Porous carbon materials as mainly electrode materials for the application in EDLC have been considerable [3-

5]. It is well known that the specific surface area directly affects the electrical energy storage of EDLC. Therefore, higher specific surface area could provide more for charge storage in EDLC. The various porous carbon materials have been successfully synthesized via using template techniques [6-8], catalytic activation[9-11], carbonization of polymer blend[12], CVD methods [13]. However, these methods have a complicated synthesis procedure or are high cost or use the some toxic reagents. Furthermore, the surface area of porous carbon is relatively low, resulting in low capacitance. Therefore, for improving surface area in practical application, physical or chemical activation has been required [14]. So far, the specific surface area of general porous carbon by chemical activation is approach $3000\text{m}^2/\text{g}$. It is not enough for electrode materials. In our research, we use two step method including rice hull carbonization and activation to prepare a series of higher special surface area porous carbon, the largest one is $3969\text{m}^2/\text{g}$. We also have drawn a conclusion that the highest specific surface area rice hull based porous carbon exhibited a super capacitance up to 368F/g at the scanning rate of 2mv/s in the cyclic voltammetry (CV) measurement and exhibited a good pseudo-capacitance behavior.

2. EXPERIMENTAL SECTION

The chemical reagent used in our experiments was of analytical grade and was used as received without further purification. Sodium hydroxide was purchased from Tianjin Damao Chemical Reagent Factory. The rice hull getting from a local village of Huaihua in Hunan province, first it was directly carbonized at 400°C in the presence of nitrogen for 2h at the rising rate of $5^\circ\text{C}/\text{min}$. Then, the carbonized rice hull was mixed with sodium hydroxide, the ratio of sodium hydroxide/ carbon was range from 0 to 6, then these carbon samples are heated to 800°C with different temperature rising segments. Thereafter, the activated products were ground, washed with distil water until the PH come near to 7, and then we dried it in 60°C oven for 12h to dehydration.

The specific surface area and pore diameter of the samples were measured by N_2 adsorption isotherm using the BET surface area of sample was measured on a Tristar 3000 (Micromeritics) by BET method. The change of element among carbonization and activation process are analyzed by Series II CHNS/O Analyze 2400.

The working electrode was prepared by pressing the mixture of rice hull based porous carbon, carbon black and 5% PTFE (75: 15: 10wt %) into a foam nickel electrode under 35 MPa. All electrochemical measurements were conducted in a standard three electrodes cell on a CHI 660B electrochemical workstation in an aqueous solution of $6\text{mol}\cdot\text{L}^{-1}$ KOH. Different sweep rates were employed in cyclic voltammetry within the range from minus 0.9V to 0.1 V vs Hg/HgO.

3. RESULTS AND DISCUSSION

Table 1 shows the composition of rice hull [15]. Silica, lignin, cellulose, protein, fat and other nutrients are the main contents of rice hull. In order to know the changes of elements among carbonization and activation, we take the contents of carbon, hydrogen and nitrogen of the product in

different preparation states, the consequences are show in Table 2. After carbonization and activation, the content of carbon in the products obviously increased, when the react time increased, the content of hydrogen decreased, but the content of carbon increased, it is mainly due to the decomposition of fibers, lignin, and cellulose.

Table 1. Main composition and content of rice hull

Main composition	Content (wt.%)
SiO ₂	18.8-22.3
Lignin	9.0-20.0
Cellulose	28.0-38.0
Protein	1.9-3.0
Fat	0.3-0.8
Nutrients after full digestion	9.3-9.5

Table 2. The changes of content of C、N、 H in the preparation process.

Samples	SBET (m ² /g)	Content (wt%)			
		C	N	H	Others
G	0.158	42.05	0.47	6.58	50.9
G4-5N0A2	400	60.23	0.81	2.51	36.45
G8-5N3B1	3049	87.69	0.04	0.35	11.92
G8-5N3C1.5	3969	91.98	0.03	0.01	7.98

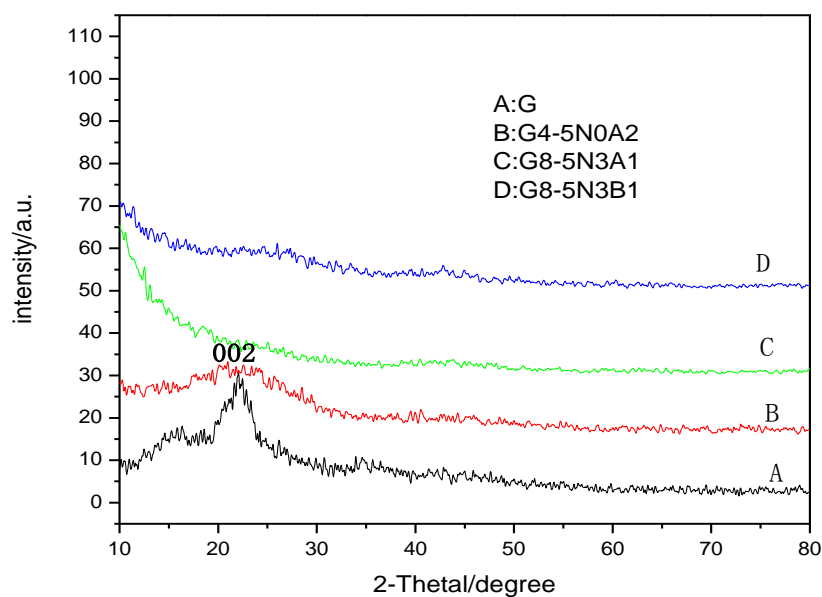
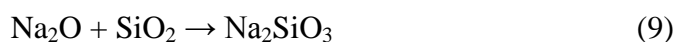
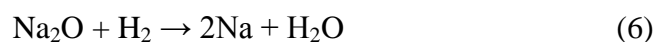
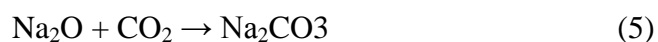
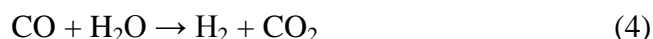
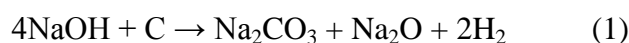


Figure 1. XRD patterns of different activation porous carbon

With the rising of temperature, the organic substances enter into the stage of polymerization and aromatization, the pyrolytic lignin formed amorphous carbon and lots of graphite-like microcrystalline carbon. With extend of react time, the react between sodium hydroxide and rice hull carbon become more completely. Moreover, the content of carbon in activation product larger than carbonization products, it is because the NaOH will continue destroy the bond C-H to form amorphous carbon, resulting in the content of carbon increased significantly and the content of hydrogen decreased.

Typical XRD pattern of different carbonizing samples is shown in Fig. 1. There is a broad peak at 23° before the activation. After dealing with sodium hydroxide, the broad peak disappears. It corresponds to the sodium hydroxide destroy rice hull's crystal texture. The results agree with the activation mechanism. In addition, with the rising of temperature, the peak at 23° become wider, it account for the temperature can also break the crystal texture in rice hull. There is no peak founded after activation suggests the presence of rice hull carbon is amorphous.

Activation mechanism between alkali hydroxide and rice hull is complicated. General speaking, the most reaction mechanism approved may be as follows [16]:



The detail BET surface area and pore distribution of different ratio of sodium hydroxide are show in Table 3.

With the ratio of sodium hydroxide/carbon increased, the corresponding specific surface area first increased and then decreased, when the ratio of sodium hydroxide/carbon is 3, the surface area of porous carbon samples(G8-5N3B1) can achieve to 3460m²/g.

Table 3. The surface area and pore-structure parameters of RH based porous carbon with different ratio of sodium hydroxide/carbon

Samples	SBET a (m ² /g)	V _{tb} (cm ³ ·g ⁻¹)	D _{BJH} e (nm)
G8-5N0B1	175	0.12	2.34
G8-5N1B1	280	0.14	2.09
G8-5N2B1	1393	0.66	3.41
G8-5N3B1	3460	1.69	2.46
G8-5N4B1	3359	2.03	2.69
G8-5N5B1	2270	1.17	2.60
G8-5N6B1	2896	1.45	2.77

When the mass ratio of sodium hydroxide/ carbon is less than 3, there are insufficient sodium hydroxide to react with rice hull charcoal, resulting in creating pore effect not obviously, so the specific surface area of rice hull based carbon don't increase significantly; when the mass ratio of sodium hydroxide/carbon is greater than 3, the excessive sodium hydroxide will continue react with chaff charcoal, leading to part of pores collapse, and some pores fuse and then form larger holes, so the specific surface area decreased.

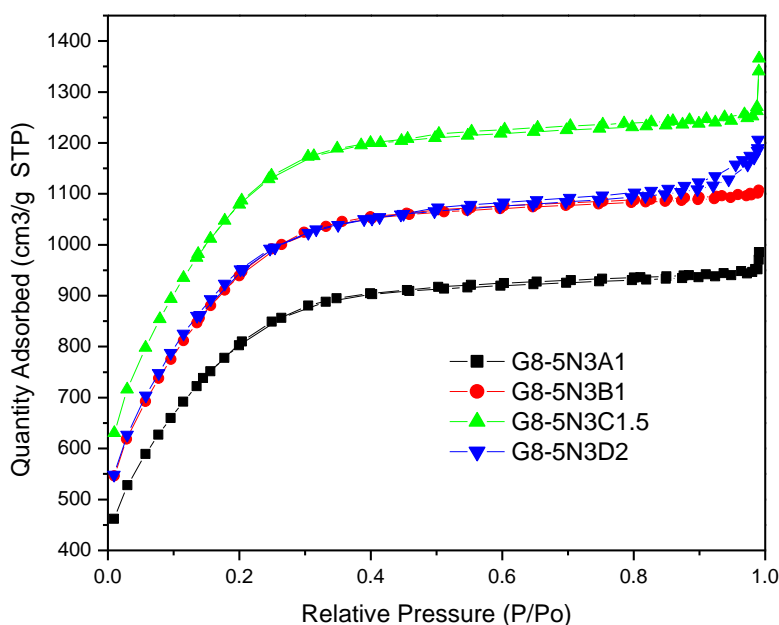


Figure 2. N₂ adsorption/desorption isotherms at 77 K on samples

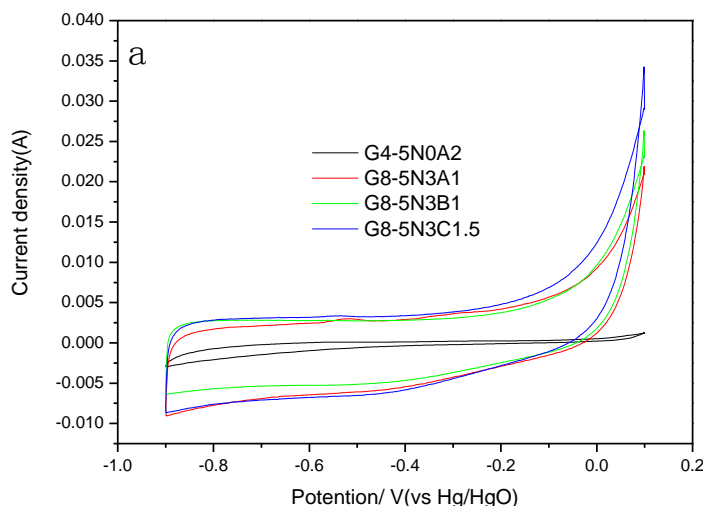
To study the influence of temperature rising segments in the activation on the nanoporous architecture formation, Nitrogen adsorption and desorption isotherms measured at 77 K are shown in Fig.2. Fig.2 indicates desorption curves are typical class I curve, which means most pores in the rice husk based porous carbon are micro pores. Before the relative pressure achieve to $P/P_0 = 0.4$, the amount of N_2 adsorption increased sharply with increasing relative pressure, but when the relative pressure pass $P/P_0 = 0.4$, the trend of the curve slow down, it is due to the holes in the porous carbon samples happened capillary condensation, the samples of N_2 adsorption capacity increased, but the rate of adsorption is slowed down significantly. The detail textural parameters are listed in Table 4.

Table 4. The surface area and pore-structure parameters of RH based porous carbon with different temperature rising segments

Samples	S_{BET} a (m^2/g)	V_{tb} ($cm^3 \cdot g^{-1}$)	D_{BJH} e (nm)
G8-5N3A1	3049	1.53	2.68
G8-5N3B1	3460	1.69	2.46
G8-5N3C1.5	3969	1.93	2.80
G8-5N3D2	3495	1.79	2.85

Table 5. The BET surface area and capacitance of rice hull based porous carbon in the scanning rate of 2mv/s

Samples	Scanning rate ($mv \cdot s^{-1}$)	capacitance ($F \cdot g^{-1}$)	BET (m^2/g)
G8-5N3C1.5	2	368	3969
G8-5N3B1	2	357	3460
G8-5N3A1	2	260	2046
G4-5N0A2	2	19	400



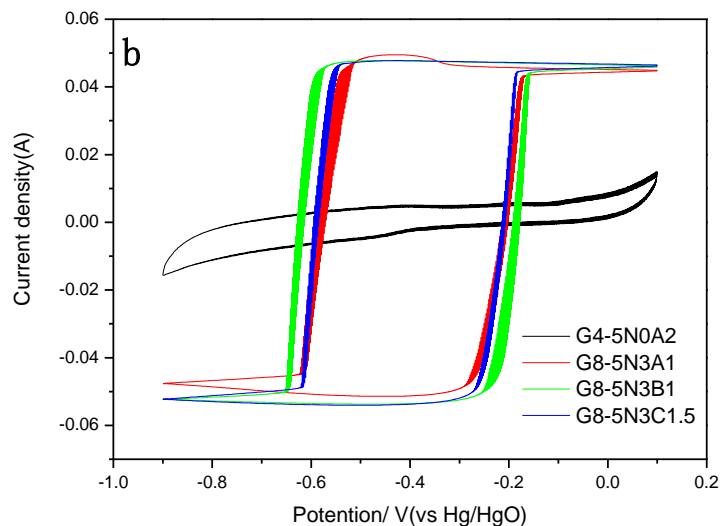
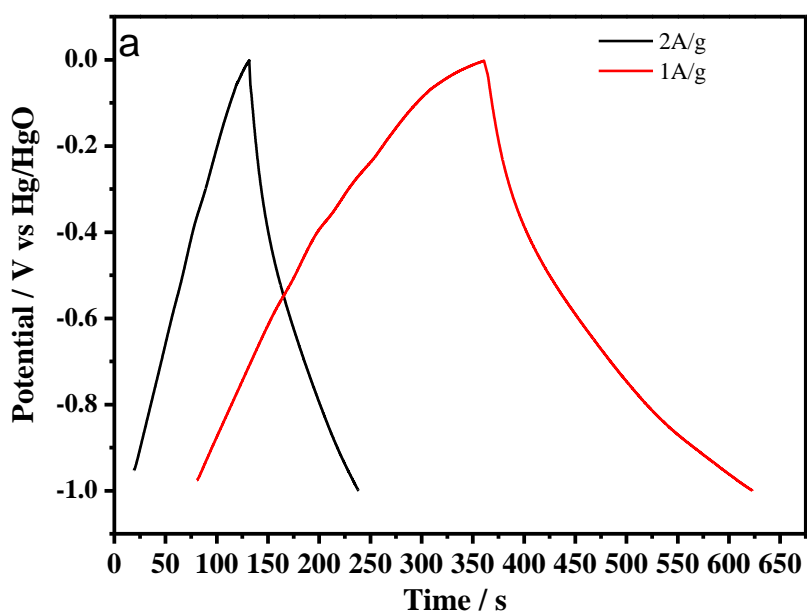


Figure 3. Cyclic voltammograms taken at scan rate of 20 mV/s (a) and 100 mV/s (b).in 6 mol·L⁻¹ KOH at room temperature

When the activation of temperature rising times increased, the specific surface area first become larger and then become smaller. It is mainly due to the reaction makes NaOH dehydrate slower and makes the body slowly swell up when the temperature rising segments increased, temperature rising segments in the activation phase has effect on the conduction of heat and gas. When the reaction between NaOH and porous carbon become more sufficient, more pores will be created. When passed the best proportion 3 segments, more pores collapsed and organic carbon was removed. Thus, the surface area of porous carbon increased.



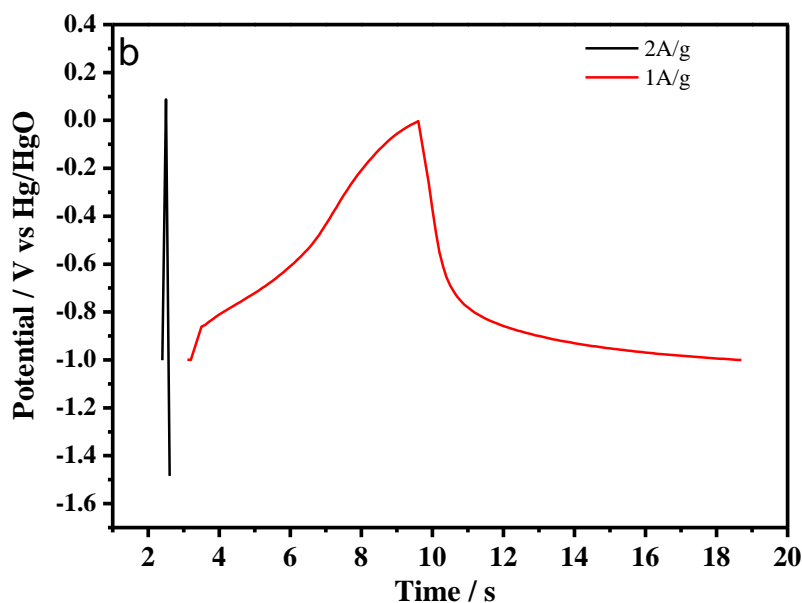


Figure 4. Galvanostatic charge/discharge curves of G8-5N3A2 (a) and G4-5N0A2 (b) at 1A/g, 2A/g.

From Fig 3b, when the scan rate is 100mV / s, the cyclic voltammetry curves were classic rectangle potential windows, suggesting porous carbon samples after activation still have good capacitance characteristics, however, G4-5N0A2 doesn't exhibit such characteristics, it indicates that the capacitance of the carbonized samples show poor capacitance, it is mainly due to the activation have big surface area and big specific pore volume, so electrolyte can easily pass the pores and touch the electrode materials. When the scan rate is 2 mV / s in Fig 3a, the cyclic voltammetry curve does not display rectangular shape except G4-5N0A2, the possible reason is pores in G4-5N0A2 under developed, its specific surface area are only $400\text{m}^2 / \text{g}$, the paths for electrolyte ions entering into the pores are short, so there is no major changes in its capacitance volume. From Table 5, the capacitance of G8-5N3C1.5 is 368 F / g, which thanks for their multi-level pore structure; the specific reason is that porosity of rice husk based porous carbon samples increased [17]. Large porosity and pore volume are conducive to the adoption of the electrolyte solution, so rice hull samples after activation have big capacitance in the low-voltage scan rate.

Figure 4a show charge-discharge curves of the electrode G8-5N3C1.5 approximate a straight line in the current density 1A / g and 2A / g, and its charge-discharge curve has the triangle symmetrical, indicating that the electrode has good performance in the analog capacitance, chemical stability and reversibility [18-19]. However, we can see from Fig 4b, the charge-discharge curves of the electrode G4-5N0A2 in the current density 1A / g and 2A / g are bent seriously, which indicates that electrochemical stability and reversibility of the carbonized samples in the current density 1A / g and 2A / g are very poor. Above all, the activation products have good chemical stability and reversibility than the carbonization products.

4 CONCLUSIONS

Rice hull was first carbonized at 400°C for 2h, and then it was mixed with NaOH with different ratio of NaOH/C from 0 to 6, and finally heating to 800°C with a unique 1 to 4 segments' temperature curve program. Thus, the porous carbons obtained had a BET surface area of 175 to 3969 m² g⁻¹ and a pore volume of 0.12 to 2.03 cm³ g⁻¹. These porous carbons have both a high pore volume and a very large specific surface area. When ratio of NaOH/C and temperature rising segments increased to 3, the surface area of rice hull based porous carbon increased rapidly. After passing this proportion, surface area begins to decrease. We can draw a conclusion that specific surface area and pore distribution changed with the transformation of the ratio of NaOH/C and temperature rising segments, and the activation products have good chemical stability and reversibility than the carbonization products, the product G8-5N3C1.5 exhibits big capacitance up to 368 F/g, which make it avail for energy storage.

ACKNOWLEDGEMENTS

This study was financially supported by the National Nature Science Foundation of China(21031001 and U0734005), and the Fundamental Research Funds for the Central Universities (21610102).

References

1. X.Y. Zeng, Y.T Ma, L.R. Ma. *Renewable and Sustainable Energy Reviews* 11 (2007) 976–987.
2. Yupeng Guo, Jurui Qi, Yanqiu Jiang, et al. *Materials Chemistry and Physics* 80 (2003) 704–709
3. M. Lazzari, F. Soavi, M. Mastragostino, *J. Power Sources* 178 (2008) 490–496.
4. J.J. Niu, W.G. Pell, B.E. Conway, *J. Power Sources* 156(2006)725-740.
5. E. Frackowiak, K. Metenier, V. Bertagna, F. Beguin, *Appl. Phys. Lett.* 77(2000)2421-2423.
6. J. Lee, S. Yoon, S.M. Oh, C.H. Shin, T. Hyeon, *Adv. Mater.* 12(2000)359.
7. J.S. Lee, S.H. Joo, R. Ryoo, *J. Am. Chem. Soc.* 124(2002)1156.
8. J.Górka, A. Zawislak, J. Choma, M. Jaroniec, *Carbon* 46(2008)1159.
9. M.Gozin, Alexander Weisman, et al. *Nature* 364 (1993)699-701.
10. J.F Sun, X.Q. Wang, Chaosheng Wang, et al. *Journal of Applied Polymer Science* 99(2006)2565
11. H. Tamon, H. Ishizaka, M. Okazaki, *Carbon* 35 (1997)791—796.
12. H.Y. Liu, K.P. Wang, H.S. Teng, *Carbon* 43 (2005) 559-566.
13. K. Kobayashi, R. Kitaura, Y. Kumai, Y. Goto, S. Imagaki, H. Shinohara, *Carbon* 47(2009)722.
14. A.G. Pandolfo, A. F. Hollenkamp, *J. Power Sources* 157(2006)11-27.
15. B.E. Conway, *Electrochemical Supercapacitors Scientific Fundamentals and Technological Application*. New York: Kluwer/Plenum; 1999.
16. H. Hatori, Y. Yamada, M. Shiraishi, et al. *American Carbon Society* 9(1995)416–417.
17. D. W. Wang, F. Li, M. Liu, et al. *Angewandte Chemie-internation Edition* 47 (2008)373-376.
18. J. Chmiola, G. Yushin, Y. Gogotsi, et al. *Science* 313 (2006)1760-1763.
19. G. Z. Gryglewicz, J. Machnikowski, E. Lorenc-Grabowska, et al. *Electrochim. Acta* 50 (2005) 1197-1206.