Available online at www.sciencedirect.com
ScienceDirect
Journal of Power Sources 160 (2006) 762–763
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Comment

Comment on "*Studies on nanoporous glassy carbon as a new electrochemical capacitor material* [Y. Wen, G. Cao, Y. Yang, J. Power Sources 148 (2005) 121–128]

Artur Braun [a,b,*]

[a] *University of Kentucky, Department of Chemical & Materials Engineering, Lexington, KY 40506, USA*
[b] *EMPA–Swiss Federal Laboratories for Materials Testing and Research, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland*

Received 30 November 2005; accepted 30 March 2006
Available online 9 June 2006

Abstract

Gas-phase activated monolithic glassy carbon was used as electrochemical double layer capacitor electrode by a research team of Siemens AG in the early 1980s [1], J. Miklos, K. Mund, W. Naschwitz, Siemens AG, Offenlegungsschrift DE 30 11 701 A1, German Patent (1980).

Wen et al. [2] (Y.H. Wen, G.P. Cao, J. Cheng, Y.S. Yang, New Carbon Mater. 18(3) (2003) 219, and [3] Y.H. Wen, G.P. Cao, Y.S. Yang, J. Power Sources 148 (2005) 121, have repeatedly questioned the performance of this glassy carbon based supercapacitor electrode concept. This asks for some comments.

Keywords: Electrochemical capacitors; Glassy carbon

Wen et al. [2,3] claim to have found in nanoporous glassy carbon a new electrochemical capacitor material. However, glassy carbon is nothing else than nanoporous per se. Hence glassy carbon and nanoporous glassy carbon mean the same. Emphasizing the well-known size range of the pores in glassy carbon does not add novelty to the material or the concept.

They also state that the Siemens researchers and those, who followed up on their approach [4,5], only turned the surface of glassy carbon into a porous structure. This is true and as a matter of fact the unique and intriguing approach of the invention: to build a monolithic and bipolar electrode assembly with separated electronically and ionically conducting layers [1,6], with emphasis on high power density. It would be nonsense to try to fully activate such monolithic glassy carbon. The unique design would not work anymore.

They also state that glassy carbon cannot be activated totally. This is not true. Activation of glassy carbon is governed by the principals of predator–prey systems and has been studied extensively [4–12]. The kinetic laws for active film thickness growth on a plate can be virtually summarized by the Generalized Lambert W function:

$$D(t) = \frac{b}{a}\left(1 + \text{LambertW}\left(-\exp\left(-1 - \frac{a^2 t}{b}\right)\right)\right),$$

where the steady state film thickness b/a is approached with a time constant $\tau = b/a^2$. Constants a and b contain the reaction and diffusion constants, respectively, as well as the temperature dependence [7,8].

Hence, a glassy carbon plate with initial thickness L will be totally activated after the time t^*, which reads

$$t^* = -\frac{\ln(-2L(a-b)/b)b + 2La}{a^2}.$$

The disappearance of the unreacted glassy carbon core is experimentally observed [4], though not desired for this particular monolithic bipolar application.

DOI of original article:10.1016/j.jpowsour.2005.02.001.
* Correspondence to: EMPA–Swiss Federal Laboratories for Materials Testing and Research, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland. Tel.: +41 44 823 4850; fax: +41 44 823 4150.
E-mail address: artur.braun@empa.ch.

0378-7753/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2006.03.083

Total activation of glassy carbon powder was performed [9], too, but for a different application [12].

Finally, the performance of glassy carbon electrodes for electrochemical capacitors in the aforementioned assembly should be judged only by their technical merit. This is done best by using a Ragone plot [13]. Several robust capacitor prototypes with various specifications were built, for instance one with 24 V and maximum energy 115 J, and maximum power 5.7 kW. For the carbon part only, the power density exceeds $50\,\mathrm{kW\,l^{-1}}$, with electrical switches being potential applications [14].

References

[1] J. Miklos, K. Mund, W. Naschwitz, Siemens AG, Offenlegungsschrift DE 30 11 701 A1, German Patent (1980).

[2] Y.H. Wen, G.P. Cao, J. Cheng, Y.S. Yang, Nanoporous glassy carbon—a new electrode material for supercapacitors. I. Effect of curing temperature on its structure and properties, New Carbon Mater. 18 (3) (2003) 219.

[3] Y.H. Wen, G.P. Cao, Y.S. Yang, Studies on nanoporous glassy carbon as a new electrochemical capacitor material, J. Power Sources 148 (2005) 121.

[4] A. Braun, M. Bärtsch, B. Schnyder, R. Kötz, O. Haas, H.G. Haubold, G. Goerigk, X-ray scattering and adsorption studies of thermally oxidized glassy carbon, J. Non-Cryst. Solids 260 (1–2) (1999) 1.

[5] A. Braun, M. Bärtsch, O. Merlo, B. Schnyder, B. Schaffner, R. Kötz, O. Haas, A. Wokaun, Exponential growth of electrochemical double layer capacitance in glassy carbon during thermal oxidation, Carbon 41 (4) (2003) 759.

[6] M. Bärtsch, A. Braun, B. Schnyder, R. Lötz, O. Haas, Bipolar glassy carbon electrochemical double-layer capacitor: 100,000 cycles demonstrated, J. New Mater. Electrochem. Sys. 2 (4) (1999) 273.

[7] A. Braun, M. Bärtsch, B. Schnyder, R. Kötz, A model for the film growth in samples with two moving reaction frontiers—an application and extension of the unreacted-core model, Chem. Eng. Sci. 55 (22) (2000) 5273.

[8] A. Braun, A. Wokaun, H.-G. Hermanns, Analytical solution to a growth problem with two moving boundaries, Appl. Math. Model. 27 (1) (2003) 47.

[9] A. Braun, M. Bärtsch, B. Schnyder, R. Kötz, O. Haas, A. Wokaun, Evolution of BET internal surface area in glassy carbon powder during thermal oxidation, Carbon 40 (3) (2002) 375.

[10] W. Gille, A. Braun, SAXS chord length distribution analysis and porosity estimation of activated and non-activated glassy carbon, J. Non-Cryst. Solids 321 (1–2) (2003) 89.

[11] A. Braun, V. Mahilingam, Activated glassy carbon for energy storage, Abstr. Pap. Am. Chem. Soc. 229: U853-U853 014-FUEL Part 1, March 13, 2005.

[12] C. Schüler, R. Kötz, Offenlegungsschrift DE 198 36 651 A1, German Patent and Trade Mark Office, 13 August 1998.

[13] T. Christen, M.W. Carlen, Theory of Ragone plots, J. Power Sources 91 (2) (2000) 210.

[14] R. Kötz, M. Bärtsch, M. Hahn, B. Schnyder, Bipolarer elektrochemischer Doppelschichtkondensator mit hoher Leistungsdichte, In: Elektrochemische Verfahren für neue Technologien, Gesellschaft Deutscher Chemiker, Frankfurt am Main, 2001, pp. 158–166 (GDCH-Monographie, Bd. 21; 2000).