Carbon materials for supercapacitor application by
dydrothermal carbonization of D-glucose

T. Tooming, T. Thomberg, T. Romann, R. Palm, A. Jänes and E. Lust
Institute of Chemistry, University of Tartu, 14 a Ravila Str., 50411, Tartu, Estonia

E-mail: thomas.thomberg@ut.ee

Abstract. Hydrothermal carbonization (HTC) of 1 M D-glucose solution was carried out in a
stainless steel autoclave, which was introduced into a tube furnace and maintained at the
temperature 260 °C for 24 hours for HTC reaction. Obtained carbonaceous materials were
pyrolyzed and activated using carbon dioxide to fine-tune the porosity of HTC carbons. Raman
spectroscopy and high resolution transmission electron microscopy data revealed that
synthesised carbon materials were mainly amorphous. Scanning electron microscopy studies
demonstrated that carbon materials were consisted of micrometer scale mainly spherically
shaped particles maintaining their shape and structure throughout pyrolysis and activation
processes. Based on the low-temperature N2 sorption experiments the specific surface areas up
to 1540 m² g⁻¹ were measured for differently activated HTC. Various electrochemical methods
were used to study influence of carbon materials physical characteristics on the supercapacitor
electrochemical performance based on HTC carbon electrodes in 1 M (C₂H₅)₃CH₃NBF₄
solution in acetonitrile.

1. Introduction

Decrease of fossil fuels resources and impact of combustion of fuels to the environment has been
forced materials chemists to develop new technologies and materials for novel energy storage and
conversion devices. Recently, some attention has been paid how to produce functional carbonaceous
materials by hydrothermal carbonization (HTC) method and various carbonaceous materials with
different particle size, shape and functionality have been synthesised [1-3]. However, these
carbonaceous materials obtained, possess only a small number of micropores and therefore have
limited micro/mesoporosity and micropore surface area. The simplest possibility to increase the
surface area and tune the pore size of carbonaceous materials is pyrolysis, where organic molecules
are removed and porosity is generated. The pore size and the surface area of the carbonized raw
powder can also be increased by using additional activation methods based on the application of air,
carbon dioxide, water steam, KOH, NaOH, H3PO4 etc. as an activation agents [4].

In the present work, activated carbons (ACs) were synthesised from D-glucose by using HTC
method followed by pyrolysis and activation with carbon dioxide at 900 °C with different activation
step lengths to prepare carbon materials with variable specific surface area, pore size distribution and
optimal ratio of micro- and mesopores for supercapacitor application [5-16]. Synthesised carbon
materials were noted as GDAC (glucose derived activated carbon). As a result of different activation
step lengths the burn-off values of 0%, 18%, 24%, 32%, 41% and 51% have been calculated and
materials were noted as GDAC-0, GDAC-1, GDAC-2, GDAC-3, GDAC-4, GDAC-5, respectively.
The electrodes were composed of an aluminium current collector and of the GDAC material layer. The GDAC material layer used was prepared from HTC carbon (94 wt%) and from the mixture of binder (6 wt%) (PTFE, 60% dispersion in H₂O). The two–electrode standard Al test cell with two identical electrodes (≈2.0 cm²) was completed inside the glove box (O₂ and H₂O concentrations lower than 0.1 ppm) and all electrochemical experiments were carried out at temperature \( T = 20 \, ^\circ\text{C} \). Carefully vacuum dried 25 \( \mu \text{m} \) thick TF4425 (Nippon Kodoshi) separator sheet was used for mechanical separation of the working electrodes from each other. Various electrochemical methods (CV, EIS, constant power discharge) were used to study the influence of carbon materials physical characteristics on the supercapacitor electrochemical performance, i.e. on the region of ideal polarizability, high and low frequency series resistance and capacitance, characteristic relaxation time constant, etc.. 1 M (C₂H₅)₃CH₃NBF₄ solution in acetonitrile (AN) has been selected as an electrolyte for GDAC based supercapacitors.

2. Experimental part and discussion

2.1. Hydrothermal carbonization, pyrolysis and activation

The hydrothermal carbonization of 50 ml 1 M D-(+)-glucose solution in H₂O was carried out in a 60 ml stainless steel autoclave. Autoclave was placed into a tube furnace, which was heated up at the rate of 10 \( ^\circ\text{C} \) min⁻¹ and was maintained at the temperature 260 \( ^\circ\text{C} \) for 24 hours for hydrothermal reaction. Thereafter, autoclave was cooled down to room temperature and the carbonaceous material was collected and washed for several times with ultra-pure (Milli-Q⁺) water. Finally, resulting carbonaceous material was dried in a vacuum oven (80 \( ^\circ\text{C} \), 100 mbar) overnight.

The dried raw HTC carbonaceous material was pyrolysed under Ar flow in a tube furnace. After the carbonization step additional activation of the samples were carried out with carbon dioxide at 900 \( ^\circ\text{C} \) with different activation step lengths. During heating up and cooling down steps the reactor was flushed with argon.

2.2. Physical characterization

The Raman spectra were recorded using a Renishaw inVia micro-Raman spectrometer using Ar laser excitation (\( \lambda = 514 \text{ nm} \)) and the fitting of the D- and G-bands were performed by the fitting of the two Lorentzian curves to the G- and D-band, respectively.

The porous structure of GDAC was characterized by using the low-temperature N₂ adsorption/desorption experiments at the boiling temperature of liquid nitrogen (≈195.8 \( ^\circ\text{C} \)) using the ASAP 2020 system. The specific surface area, micropore surface area (\( S_{\text{micro}} \)), micropore volume (\( V_{\text{micro}} \)) and total pore volume (\( V_{\text{tot}} \)) and other parameters for porous carbon materials were calculated according to the Brunauer-Emmett-Teller and t-plot method. The pore size distribution was determined using non local density functional theory assuming a slit-shaped pores model [7-9,13,16].

![Raman spectra and differential pore size distribution](image)

Fig. 1. Raman spectra (a) and differential pore size distribution vs pore width plots (b) for different porous GDAC materials.
2.3. **SEM and HRTEM data for GDAC materials**

The surface structure and morphology of HTC carbons was examined by scanning electron microscopy (SEM) method using a FIB–SEM Helios™ Nanolab 600 system and high resolution transmission electron microscopy (HRTEM) using a Tecnai 12 instrument operated at a 120 kV accelerating voltage, respectively.

![SEM and HRTEM images](image)

**Fig. 2.** SEM (a) and HRTEM (b) images for porous GDAC materials.

As shown in Fig. 2a, the carbon produced from 1 M D-(-)-glucose solution exhibited interconnected spheres with a narrow size of about 1.0 µm and relatively smooth surface structure. After activation, the spheres size reduced only slightly as a result of burn-off of carbon during activation step. Fig. 2b, exhibit the HRTEM image for porous GDAC-5 prepared during activation, show small segments of curved graphene monolayers with no evidence of interlayer connection corresponding to mainly amorphous carbon. From the HRTEM image, it is clear, that there is no obvious change in GDAC structure and activation has practically no influence on the crystal structure, which are in a good agreement with powder Raman spectroscopy results (Fig. 1a).

2.4. **Specific energy and power, Ragone plots**

The specific energy \(E\) and power \(P\) relationship, i.e. Ragone plots (calculated to the total active material weight of two electrodes), for the supercapacitors based on GDAC electrodes have been obtained from constant power tests within the cell potential range from 3.0 V to 1.5 V and are shown in Fig. 3.

![Ragone plots](image)

**Fig. 3.** Ragone plots for the supercapacitors completed using different GDAC electrodes in 1 M \((\text{C}_2\text{H}_5)_3\text{CH}_3\text{NBF}_4 + \text{AN}\) solution, obtained from constant power tests within the cell potential range from 3.0 V to 1.5 V.
The Ragone plots for GDAC materials, having different porosity, micropore and total pore volume, pore size distribution, etc., show noticeable influence of activation condition on the stored energy and delivered power values. Stored energy values for supercapacitors were increased with the increase of the average pore width, because all pores are accessible for partially desolvated ion adsorption, and can be applied for effective energy storage. GDAC materials with higher porosity and larger average pore width (Fig. 1b) ensure fast ions transport in pores and deliver higher power at constant energy. These energy and power values are even higher compared with values established for supercapacitors based on WC–CDC (tungsten carbide derived carbon) electrodes in the same electrolyte system [16], thus, showing excellent characteristics for electrode materials applicable for ultra-high rate supercapacitor devices.

3. Conclusions
Comparison of the data for the cells completed using different GDAC electrodes indicated a strong influence of the electrode material activation conditions (i.e. porosity characteristics) on the relaxation time constant $\tau_R$ values decrease with increasing of the average pore size and decrease of the pore resistance of electrolyte in micropores. The Ragone plots for GDAC material with different micropore and total pore volume, pore size distribution etc. showed noticeable dependence of the stored energy and delivered power values on the conditions of the activation step. Stored energy and delivered power values for supercapacitors based GDAC materials were increased with increase of average pore width, because all pores are accessible for partially desolvated ion adsorption, and can be applied for effective energy storage. GDAC materials with higher porosity and larger average pore width ensure fast ions transport in pores and deliver higher power at constant energy. Thus, the energy and power values established for supercapacitors based on GDAC electrodes in 1 M (C$_2$H$_5$)$_3$CH$_3$NBF$_4$ in acetonitrile solution show excellent characteristics applicable for ultra-high power devices.

Acknowledgements
This work was supported by the Estonian Science Foundation under Projects Nos. 8172 and 9184, Estonian Ministry of Education and Research project SF018002s08, European Regional Development Fund Project SLOKT10209T and Estonian Centre of Excellence in Research Project TK117 3.2.0101-0030 "High-technology Materials for Sustainable Development".

References
[1] Titirici M M, White R J, Falco C and Sevilla M 2012 Energy Environ. Sci. 5 6796
[2] Sevilla M and Fuertes A B 2009 Chem. Eur. J. 15 4195
[3] Li M, Li W and Liu S 2011 Carbohydrate Research 346 999
[4] Marsh H and Rodriguez-Reinoso F 2006 Activated Carbon (Elsevier, Amsterdam)
[5] Thomberg T, Jänes A and Lust E 2009 J. Electroanal. Chem. 630 55
[6] Thomberg T, Jänes A and Lust E 2010 Electrochim. Acta 55 3138
[7] Thomberg T, Kurig H, Jänes A and Lust E 2011 Micropor. Mesopor. Mater. 141 88
[8] Tallo I, Thomberg T, Kontturi K, Jänes A and Lust E 2011 Carbon 49 4427
[9] Tallo I, Thomberg T, Kurig H, Jänes A, Kontturi K and Lust E 2013 J. Solid State Electrochem. 17 19
[10] Eskusson J, Jänes A, Kikas A, Matisen L and Lust E 2011 J Power Sources 196 4109
[11] Laheäär A, Jänes A and Lust E 2011 Electrochim. Acta 56 9048
[12] Laheäär A, Jänes A and Lust E 2012 Electrochim. Acta 82 309
[13] Jänes A, Thomberg T, Kurig H and Lust E 2009 Carbon 47 23
[14] Jänes A, Permann L, Arulepp M and Lust E 2004 J. Electroanal. Chem. 569 257
[15] Tõnurist K, Jänes A, Thomberg T, Kurig H and Lust E 2009 J. Electrochem. Soc. 156 A334
[16] Tallo I, Thomberg T, Jänes A, Kontturi K and Lust E 2012 J. Electrochem. Soc. 159 A208