

# CARBON/IODIDE INTERACTIONS FOR SUPERCAPACITOR APPLICATIONS

*Elzbieta Frackowiak, Grzegorz Lota and Krzysztof Fic*

Institute of Chemistry and Technical Electrochemistry,  
Poznan University of Technology,  
60-965 Poznan, Piotrowo 3, Poland

## Introduction

Electrochemical double layer capacitors (EDLCs) are high power energy sources, very attractive for hybrid application because of fast energy delivery and long durability. Performance of capacitor is based on electrostatic attraction of ions in the electrode/electrolyte interface. In the charged state, a supercapacitor is equivalent to two cells of capacities  $C_1$  and  $C_2$  in series. The capacity of total system ( $C$ ) is determined by the electrode with the smaller capacity value. Hence, the selection of two electrodes with a comparable capacitance is crucial. Apart of electrostatic attraction of ions, some pseudocapacitive effects, e.g. redox reactions connected with heteroatom presence in the carbon matrix (nitrogen, oxygen), metal oxides, conducting polymers, electrosorbed hydrogen can be a source of great capacitance improvement. Generally, redox reactions take place in the bulk of electrode, however, in our innovative carbon/iodide system the main redox processes involve electrolyte solution. We already proved that the porous structure of carbon plays an important role in the faradaic processes of iodine redox couples taking place in the electrode-electrolyte interface [1]. In this paper, the further work connected with improvement of this novel concept will be presented.

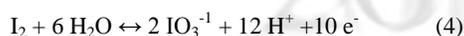
## Experimental

Electrochemical experiments have been performed in KI aqueous solutions with different concentrations ( $1\text{ mol L}^{-1}$  -  $5\text{ mol L}^{-1}$ ). For some experiments  $1\text{ mol L}^{-1}$  sulfuric acid was applied for comparison. All the capacitance measurements have been performed with an activated carbon (AC1) prepared by alkali activation (C:KOH ratio equal to 1:4) of commercially available carbon Norit® SX2. BET surface area ( $S_{\text{BET}}$ ) was estimated by ASAP 2020 (Micromeritics) and it was equal to  $2522\text{ m}^2\text{ g}^{-1}$ . The average pore size of this carbon was  $1.36\text{ nm}$  and the carbon content was  $92.5\text{ wt}\%$ . Typically microporous carbon tissue (BET specific surface area  $1617\text{ m}^2\text{ g}^{-1}$ ) was used for comparison (AC2). The electrodes for supercapacitor contained  $85\text{ wt}\%$  of carbon,  $10\text{ wt}\%$  of binder (PVDF Kynar Flex 2801) and  $5\text{ wt}\%$  of acetylene black in the case of powdered carbon material. They were prepared in the form of pellets ( $8\text{-}12\text{ mg}$ ) with a surface area of  $0.8\text{ cm}^2$ . Electrochemical investigations have been performed in Swagelok® system using different current collectors (gold, stainless steel). The capacitance properties (expressed per mass of one electrode) have been studied by voltammetry cycling ( $1\text{-}100\text{ mVs}^{-1}$ ), galvanostatic charging/discharging ( $10\text{ mA g}^{-1}$ - $50\text{ mA g}^{-1}$ ) and impedance spectroscopy ( $1\text{ mHz}$ - $100\text{ kHz}$ ) using VMP2/Z Biologic, AUTOLAB 30FRA2

potentiostat/galvanostats. For estimation of ions size an advanced molecular simulation has been done by DFT calculation method with Gaussian 03W software, B3LYP functional and 6-311G basis set considering fuzzy charge of molecules.

## Results and Discussion

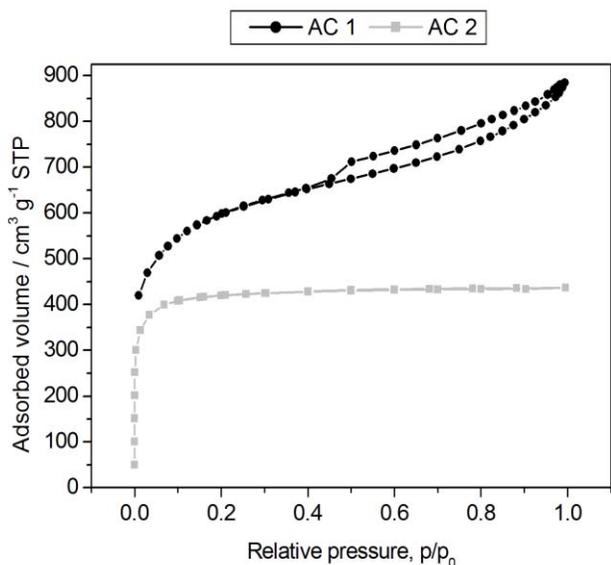
Capacitors investigated in this study were built with carbon electrodes immersed in the iodide electrolytes. The aqueous carbon/iodide system has a great advantage because it is inert, neutral and environment friendly. Energy storage had both electrostatic and faradaic origins. The iodine redox couples demonstrate a good reversibility, allowing a perfect cycling of supercapacitor to be reached. The region of electrochemical stability of iodine/water system can be easily seen from Pourbaix diagram. Close to pH equal to 7 a rich variety of possible reactions of iodine is possible from  $-1$  to  $+5$  oxidation states. All possible reactions which can proceed in the electrode/electrolyte interface during operation of the capacitor are presented.



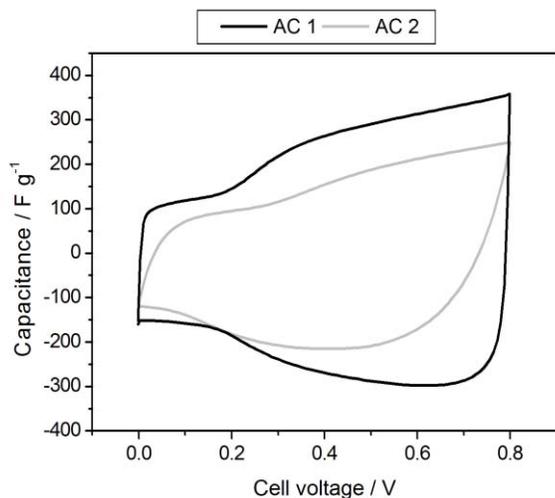
Taking into account that ions can form polyions such as  $\text{I}_3^{-}$ , eventually  $\text{I}_5^{-}$  and that they are solvated (even if iodides has limited tendency to solvation) it is obvious that microporous carbon material would be optimal but preferably with supermicropores and small mesopores presence.

In our previous work a low BET surface area carbon (Norit  $835\text{ m}^2\text{ g}^{-1}$ ) was used and we have found that the textural properties of carbon play an important role for the capacitor performance because of the redox processes of  $\text{I}^{-1}/\text{I}_2$  couple in the electrode/electrolyte interface [1]. Indeed this carbon with a limited porosity pointed out very moderate capacitance values (below  $100\text{ Fg}^{-1}$ ) showing that developed interface is crucial for a good capacitor performance with iodides. On the other hand, selecting carbon with a developed porosity (AC1 -  $2522\text{ m}^2\text{ g}^{-1}$ ) our two-electrode system gives  $280\text{ Fg}^{-1}$  and even a single positive electrode exceeds values of  $1800\text{ Fg}^{-1}$ . To explore the effect of porosity, different carbons have been used for electrochemical testing. Two carbons with a significant micropore volume over  $0.6\text{ cm}^3\text{ g}^{-1}$  but different mesopores amount were used. Their physicochemical properties are characterized by nitrogen sorption at  $77\text{ K}$  (Fig.1). In a typical microporous carbon (AC2 - lack of hysteresis in the isotherm) the mesopores amount is negligible ( $0.026\text{ cm}^3\text{ g}^{-1}$ ) whereas supermicropores as well as mesopores are observed for AC1. If only micropores would be responsible for capacitance performance of these carbons in  $1\text{ mol L}^{-1}$  KI, the capacitor performance would be quite similar. However, the presence of mesopores is crucial taking into account the size of polyiodide ions. For estimation the magnitude of ions (solvated and non-solvated) present in

electrolytic solutions an advanced molecular simulation was applied. The size of  $I^{-1}$  is 0.39 nm, whereas for  $I_3^{-}$  is 0.63 nm ( $I_3^{-}$  solvated by 4 water molecules is 1.8 nm), for  $I_5^{-}$  with irregular shape the longer part is 1.26 nm and shorter one 1.20 nm, hence, the total length exceeds 2 nm. Oxidized species such as  $IO_3^{-}$  have dimension of 0.57 nm and  $IO_3^{-}$  solvated by 3 water molecules 1.4 nm. Fig. 2 shows a capacitance comparison for these two carbons estimated by voltammetry method. It can be easily observed how crucial role plays supermicropores and mesopores presence for capacitance values and charge propagation.

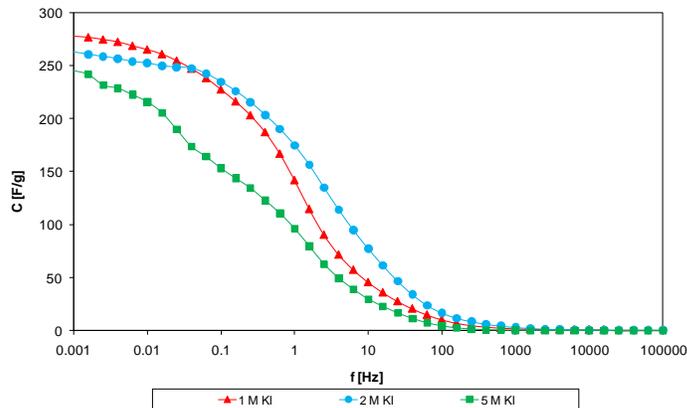


**Fig. 1** Nitrogen sorption/desorption isotherms for two carbons AC1 and AC2 used for capacitor testing



**Fig. 2** Cyclic voltammograms ( $10 \text{ mV s}^{-1}$ ) for supercapacitor carbon electrodes operating in  $1 \text{ mol L}^{-1}$  KI solution ( $234 \text{ F g}^{-1}$  for AC1 and  $146 \text{ F g}^{-1}$  for AC2)

The most frequently  $1 \text{ mol L}^{-1}$  KI has been used as electrolyte, however, higher concentrations of KI were also considered. Surely  $5 \text{ mol L}^{-1}$  KI concentration is too high what is well proved by impedance spectroscopy measurements. In this case charge propagation already aggravates at frequency of  $10 \text{ mHz}$  whereas concentration of  $2 \text{ mol L}^{-1}$  KI seems to be optimal (Fig. 3)



**Fig. 3** Impedance spectroscopy measurements in three different KI solutions

Further improvement of our system was connected with an application of the second redox couple which operates in the more negative range of potential. A great enhancement of capacitor performance in the full voltage range was obtained (over  $400 \text{ F g}^{-1}$  at a high current load ( $1 \text{ A g}^{-1}$ )).

### Conclusions

The application of carbon/iodide electrochemical system is very original and it is a significant breakthrough in supercapacitor development. The bi-functional iodide electrolyte, which ensures ionic conductivity and supplies pseudo-capacitive effects, has a great advantage due to its inertness. Among three different KI concentrations,  $2 \text{ mol L}^{-1}$  seems to be optimal. Taking into account cost and availability of different alkali metals, KI is preferable. A good reversibility of different iodine redox couples allows reaching perfect cycling. Striking values 10 times exceeding typical capacitance values are observed for the positive electrode but the negative electrode imposes the final capacitor performance. The further capacitor optimization was obtained by introducing the second redox couple based on different element. Undoubtedly, practical application of the stable reversible reactions based on iodide/iodine and other redox couples is relevant for supercapacitor progress. It has been proved how important is selection of activated carbon material with the presence of supermicropores and mesopores to reach a high charge propagation.

**Acknowledgment.** Acknowledgments are made to the Ministry of Science and Education (Poland) - grant DS 31-203/2010.

### References

[1] Lota G., Frackowiak E. Striking capacitance of carbon/iodide interface. *Electrochem. Commun.* 2009;11:87-90.