

ENHANCEMENT OF CARBON/ELECTROLYTE INTERFACE BY SURFACTANTS FOR ELECTROCHEMICAL APPLICATIONS

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Introduction

Energy storage in supercapacitors is realized by a fast electrostatic accumulation of charge in the electrode-electrolyte interface. According to formula $C = \epsilon S/d$, where C is capacitance, ϵ is dielectric constant, S electrochemically available surface area and d is the thickness of electric double layer (usually equal to 1 nm), development of the interface seems to be the most effective way to improve the capacitance. Activated carbons, as mainly used supercapacitor electrode materials [1,2], have specific surface area above $2000 \text{ m}^2 \text{ g}^{-1}$ but their capacitance is still relatively low. It may suggest that a part of this surface area is inert in the charge storage. It can be caused by hydrophobic character of carbon surface and its weak wettability by aqueous electrolytic solutions. Hence, improving wettability seems to be a reasonable approach for more efficient use of the total carbon surface. This work is focused on the enhancement of carbon electrode wettability for good electrolyte penetration to maximize electrode/electrolyte interface, in turn, charge accumulation. For better wettability small amounts of surfactants (anionic, cationic and non-ionic) as electrolyte additives were used. These compounds reveal many interesting properties, but in supercapacitor application a surface tension lowering seems to be the most important.

Experimental

Two-electrode capacitors were assembled in a Swagelok® system with pellets of comparable mass. The electrode was composed of 85 wt.% of carbon which was fully characterized in ref. [2], 10 wt.% of polyvinylidene fluoride (PVDF Kynar Flex 2801) and 5 wt.% of acetylene black. Briefly, commercial carbon Norit® XS32 was activated by KOH (1:4) giving material (AC1) with microporous surface area of $1400 \text{ m}^2 \text{ g}^{-1}$, micropore volume of $0.96 \text{ cm}^3 \text{ g}^{-1}$ and average micropore width 1.36 nm (Fig. 1). Electrodes were prepared in the form of pellets (7–10 mg) with a surface area of 0.8 cm^2 and thickness ca. 0.3 mm. The investigations were performed in acidic ($1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$), basic ($6 \text{ mol L}^{-1} \text{ KOH}$) and neutral ($1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$) solutions using gold current collectors to avoid corrosion and to preserve comparable experimental conditions. As electrolyte additives, three kinds of surfactants in a very small concentration 0.005 mol L^{-1} were used: sodium and lithium dodecyl sulphate (called briefly SDS and LDS, Sigma-Aldrich) as an anionic surfactants, tetrapropylammonium bromide and iodide (TPAB and TPAI, Sigma-Aldrich) as a cationic surfactants and polymer of polyethylene glycol and *p*-*t*-octylophenol (called TRITON X-100, Sigma-Aldrich) as non-ionic surfactant (Fig. 2).

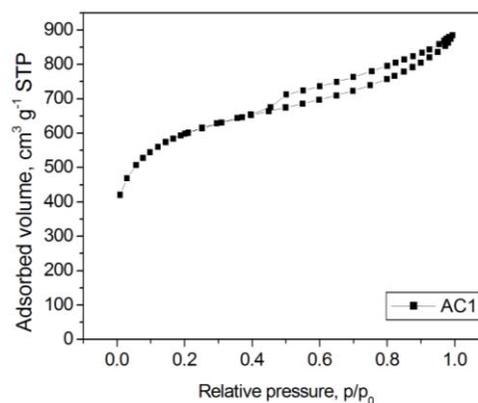


Fig. 1 Nitrogen adsorption (77K) isotherm of the activated carbon.

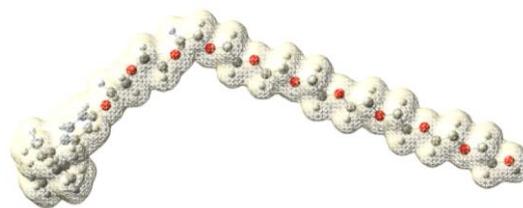


Fig. 2 Molecular structure of TRITON X-100.

Such small concentration was applied especially to overcome surfactant tendency to create aggregates consisting of large number of the molecules (called micelles). This phenomenon occurs only above critical micellar concentration (CMC), and these micelles due to their dimensions may block the pores in carbon structure what is undesirable. The molecule dimensions were calculated by DFT method using Gaussian 03W software [3]. Thanks to this calculation it was possible to determine a potential carbon – surfactant interaction or eventual pore blocking which can affect capacitance values. A glassy fibrous material played the role of separator. The capacitance properties of the composite materials (expressed per active mass of a single electrode) were studied by galvanostatic cycling at current densities from 0.2 to 50 A g^{-1} , cyclic voltammetry at voltage scan rates from 5 to 100 mV s^{-1} and electrochemical impedance spectroscopy in the frequency range from 1 mHz to 100 kHz using multichannel potentiostat/galvanostat VMP3/Z Biologic, France. Apart from capacitor measurements, electrochemical hydrogen storage was investigated in a three-electrode system. Carbon pellet was a working electrode, nickel foil served as a counter electrode and reference electrode was Hg/HgO system. Hydrogen storage process into carbon electrodes was investigated by galvanostatic charge/discharge process and by cyclic voltammetry with different regimes on the same apparatus as described above in electrolytes without and with surfactants.

Results and Discussion

Three electrochemical methods have been used for detailed characterization. Galvanostatic cycling method in a wide range of current densities was applied to determine the influence of surfactant addition on the capacitance properties. For small current densities (e.g. below 1 A g^{-1}) the change in capacitance is not significant, both for acidic, basic and neutral medium. Investigations at higher current densities (50 A g^{-1}), particularly for basic medium modified by TRITON and TPAI addition, reveal significant improvement in capacitance which is almost two times higher than for electrolyte without surfactant. This behavior suggests that surfactants may improve the dynamic of charge propagation.

Cyclic voltammetry was applied using various potential scan rates as well gradually wider operating voltage range, to elucidate capacitance properties and to compare them with the results observed during galvanostatic cycling. Almost ideal rectangular shape of voltammograms proved that certain surfactant addition improves the charge propagation even at high scan rates. Usually, for charge/discharge at high regimes some kind of distortion of box-like shape appears. A perfect voltammetry curve is a proof that electrical double layer charging/discharging process is fast and occurs without any significant ohmic drop. These results may imply that in the electrolyte modified by surfactant addition, the ions can move faster and also can occupy much more electrochemical active sites on carbon surface. Rectangular shape and lack of peaks on the voltammograms may suggest that surfactants remain stable in applied potential window. These observations are also confirmed by symmetric shape of galvanostatic charging-discharging curves. The most significant improvement of supercapacitor behavior is obtained for non-ionic surfactant in basic medium what is confirmed by all electrochemical methods. Electrochemical impedance spectra reveal much better charge propagation (almost stable on the level over 100 F g^{-1} in frequency range from 1 mHz to 10 Hz) for supercapacitor operating in basic medium modified by TRITON addition. Interesting results were obtained also for supercapacitors operating in voltage range higher than water decomposition voltage. Theoretically, supercapacitors with aqueous electrolytes can operate in voltage window smaller than 1.23 V because of electrolyte decomposition. Energy of supercapacitors, which is proportional to capacitance and square of operating voltage, are relatively low in aqueous medium. Hence, commercially available supercapacitors usually operate in organic electrolyte reaching 2.7 V , however, this medium is not environment friendly. Thanks to surfactant addition, particularly non-ionic, supercapacitors with aqueous electrolyte can operate in wider voltage window. Voltammetry curves for supercapacitor operating in $6 \text{ mol L}^{-1} \text{ KOH}$ modified by TRITON X-100 are shown in Fig. 3. It is clearly seen that there is no peak responsible for electrolyte decomposition above 1.2 V . This remarkable extension of operating voltage may be caused by the fact that electrolyte with lower surface tension can create a thin film on pore walls and the pressure in pores is too high to allow hydrogen or

oxygen evolution. Additionally, supercapacitor operating at 1.5 V after 2500 cycles of galvanostatic charging/discharging process (at current load of 1 A g^{-1}) did not point out any significant decrease of capacitance.

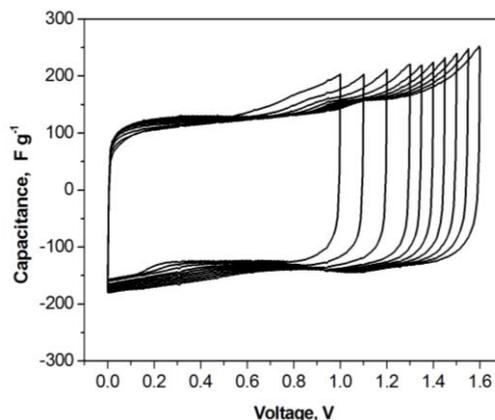


Fig. 3 Cyclic voltammetry for capacitor operating in $6 \text{ mol L}^{-1} \text{ KOH}$ with non-ionic surfactant TRITON X-100. Scan rate 10 mVs^{-1} . Gradual extension of voltage range every 100 mV .

Conclusions

The detailed study of capacitor as well as single electrodes have been performed to determine the influence of different kind of surfactant addition in $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, $6 \text{ mol L}^{-1} \text{ KOH}$ and $1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ aq. solutions. It is reported that each kind of surfactant both in acidic and alkaline medium has a positive influence on supercapacitor behavior. However, the most significant improvement was observed for KOH medium, where the higher capacitance, fast and stable charge propagation, smaller leakage current and self-discharge value as well as the wider operating voltage range was shown, particularly for non-ionic surfactant (TRITON X-100). The amount of surfactant additive higher than critical micellar concentration significantly blocks the pores entrance, in turn, a twofold decrease of capacitance has been found. The profitable concentration of surfactants was 0.005 mol L^{-1} [4]. Contrary to a positive effect of surfactant on capacitor performance, for electrochemical hydrogen storage effect of surfactant additive was rather negligible.

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