"Green" carbon for energy storage systems in non-aqueous electrolytes

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Introduction:

The nanostructured carbon-based materials fabricated from renewable bio-resources have great potential in the rechargeable energy storage systems - a modern, inexpensive and affordable approach. Carbon is one of the most abundantly available and structurally diverse materials, and most present-day EDLCs employ porous carbons as the active electrode material. Abundantly available organic materials such as coconut shells, charcoal, nut shells, wood, and food waste are a particularly attractive natural resource for the commercial production of porous carbon materials (Rufford T.E *et al*, 2008). The coconut shell produces nanostructured carbon with a relatively low internal resistance and good electrical conductivity properties, which determines their potential in the rechargeable energy storage systems.

It is found that activated carbon having higher content of acidic groups and narrow pore size distribution displays an impressive cycling stability in alkaline electrolyte solution. In our previous work, two types of bio activated carbons (YP-50F and YP-80F) were investigated and the obtained results showed that the activated carbon YP-50F having higher content of acidic groups and narrow pore size distribution displays an impressive cycling stability in alkaline electrolyte solution (B. Karamanova *et al*, 2019).

The improvement of the supercapacitor performance can further be achieved by the appropriate selection of the electrolyte composition (C. Zhong *et al*, 2015). In general, the desirable properties of an electrolytic system for supercapacitors are: high ionic conductivity, wide voltage window, and high electrochemical and thermal stability, low viscosity, low toxicity, low cost, etc (G. P. Wang *et al*, 2012).

Aqueous electrolytes have a limited cell voltage window and most commercial electrochemical capacitors use organic electrolytes instead of aqueous electrolytes (P. Hall *et al*, 2010). It is known that the higher operation voltage will give rise to a significant improvement of energy density, because it is proportional to the square of the operation voltage. Therefore, replacing conventional aqueous electrolytes (1 V) with organic electrolytes (2.7 V) is highly desirable for high-energy-density supercapacitors (Xidong Lin *et al*, 2018).

Ionic liquids are becoming more and more popular in modern green technologies and more widely used as electrolytes in supercapacitors. Electrochemical and thermal resistance; wide volt window (up to 4V); suitable mechanical stability; low flammability; environmentally friendly and others.

Therefore the proper selection of a potential window is essential for optimal performance of the supercapacitor. Cyclic voltammetry is usually performed to obtain a general picture of the behaviour of an electrochemical system, this method involves potential modulation at a rated V/dt between two potential limits, ΔV (V1 and V2).

The present work reports new data on the application of "green" carbon, obtained by pyrolysis of coconuts, as electrode material for energy systems in non-aqueous media – $LiBF_4$, $LiPF_6$ and $NaPF_6$ and ionic liquids (with and without polymer additive). The potential limits are defined and the structure and morphology changes of the electrode in the pristine form and after electrochemical testing in the different electrolytes are monitored by *ex-situ* XPS and SEM measurements.

Experimental:

The commercial activated carbon (YP-50F, "Kuraray Europe" GmbH) were used to fabricate electrodes for supercapacitor cells for electrochemical measurements. The symmetric supercapacitor cell contains two identical coin type electrodes from activated carbon (AC) and different electrolytes – $LiBF_4$ with solvent ethylene carbonate/dimethyl carbonate mixture 1:1, $LiPF_6$ and $NaPF_6$ with with solvent propylene carbonate) and ionic iquid $EMIMBF_4$ (with and without synthesized polymer additive PIL). By adding a binder – PVDF to the electrode materials, a paste is formed, which is glued to Al foil discs. The formed sheet electrodes were dried in vacuum at 80 ^oC for 12 hours and pressed under pressure of 20 MPa. The obtained electrodes were mounted in the electrochemical cell with Watman separator and filled with electrolyte in a dry box under argon atmosphere. The reference electrode was Li/Li^+. All measurements were performed at room temperature.

The cyclic voltammetry measurements (CV) were carried out in a three-electrode cell, in a voltage window from 0,8 V up to 4 V and different scan rate - from 1 mVs^{-1} up to 100 mVs^{-1}.

The structure and morphology changes in the composite electrodes after supercapacitor testing were analyzed by means of *ex-situ* XPS and SEM techniques.

Results and discussion:

The assembled three electrode cells with different organic electrolytes are electrochemically examined using cyclic voltammetry. Figure 1 shows the CV-curves in $LiBF_4$ at different scan rates - 10, 25 and 100 mVs^{-1}. As one can see, the supercapacitor has the best electrochemical capacitance performance within potential range 1,3–3.0 V. The SC cell in the other two electrolytes ($LiPF_6$ and $NaPF_6$) show optimal performance in wider potential window, and for $NaPF_6$ he is the widest (1,0 – 3,6 V). These results are confirmed by the calculated capacitance values from the cyclic voltammograms.

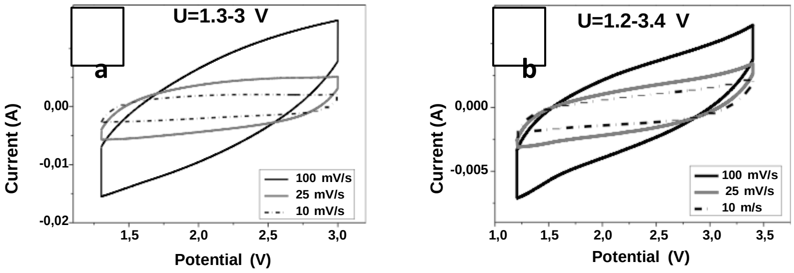

Fig. 1 CV curves of symmetric supercapacitor in $LiBF_4$ at different scan rates in potential range from 1,3 to 3,0 V(a) and CV curves in the potential range from 1,2 to 3,4 V (b)

To explain the effect of the electrolyte on the supercapacitor performance, ex-situ XPS and SEM measurements are undertaken. Figure 2 compares the SEM images of the pristine electrode and the electrode cycled in $LiBF_4$ electrolyte. The SEM image of the pristine electrode displays a formation of relatively homogeneous and dense surface and after the cycling the initial electrode surface maintains its dense shape. This indicates that the carbon electrode retain its integrity in $LiBF_4$ electrolyte. After electrochemical testing in $LiPF_6$ and $NaPF_6$, a change in the electrode structure is observed that is most significant for $LiPF_6$ electrolyte. The *ex-situ* XPS analysis show similar results.

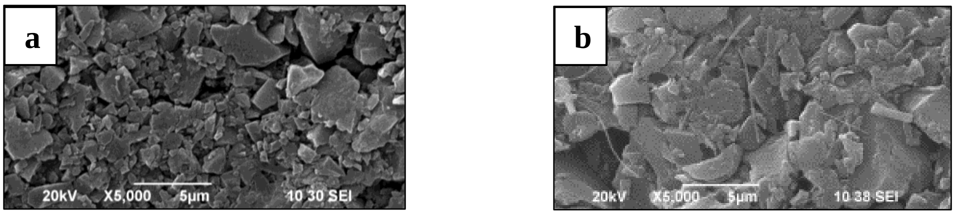

Figure 2. SEM images of the pristine AC electrode (a) and AC electrode after CV- test in $LiBF_4$ electrolyte (b)

Conclusions

The present study shows that the potential window in which the supercapacitor operates depends on the electrolyte stability. The correct determination of potential limits is essential for achieving optimal SC performance and high energy density. The results obtained are a good prerequisite for future research and for a more complete elucidation of the processes occurring in various organic electrolytes and ionic liquids (with and without polymer additive).

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