



# New design of electric double layer capacitors with aqueous LiOH electrolyte as alternative to capacitor with KOH solution

Izabela Stepniak\*, Aleksander Ciszewski

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

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## ABSTRACT

Activated carbon (AC) fiber cloths and a hydrophobic microporous polypropylene (PP) membrane, both modified with lithiated acetone oligomers, were used as electrodes and a separator in electric double layer capacitors (EDLCs) with aqueous lithium hydroxide (LiOH) as the electrolyte. Electrochemical characteristics of EDLCs were investigated by cyclic voltammetry (CV), galvanostatic charge–discharge cycle tests and impedance spectroscopy (EIS), compared with a case of the capacitor with aqueous potassium hydroxide (KOH) as an electrolyte. As a result, the capacitor with LiOH aqueous solution and a modified separator and electrodes was found to exhibit higher specific capacitance, maximum energy stored and maximum power than that with KOH aqueous solution.

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## 1. Introduction

The importance of energy storage devices has been constantly growing with the recently increasing popularity of various portable electronic devices and motor vehicles. One type of such energy storage devices are electric double layer capacitors (EDLCs), relatively new electrochemical energy storage media with a somewhat lower specific energy, but much higher specific power and longer cycle life than most rechargeable batteries [1–3]. While the storage of electric charges in batteries is based on reversible Faradic electrode reactions, in capacitors it occurs in the electric double-layer at the electrode/electrolyte interface. Therefore, they are often fabricated from activated carbons (ACs), which exhibit a high specific surface area of the order of  $10^3 \text{ m}^2 \text{ g}^{-1}$  [4]. However, specific capacitances obtained from carbon materials are usually much lower than expected. This is primarily attributed to poor wettability of the electrode material in electrolyte solution, which results in a less accessible surface area for the formation of the electric double layer; that brings about high resistance to the transport of electrolyte ions within micropores of porous carbon during charge/discharge processes. Therefore, it is mandatory for electrode material to have good wettability in the electrolyte solution if good EDLC performance is expected. This explains why several treatments have been proposed to increase their specific capacitance, such as polymer deposition [5,6] or physical/chemical activation [7,8]. To achieve high specific power

and energy as well as a long cycle life, EDLC engineering is crucial.

It is worth mentioning that generally, in an EDLC, positive and negative electrodes are identical. In order to increase energy density, a long cycle life and a fast charge capability, asymmetric cells consisting of different types of positive and negative electrodes have been introduced. Recently, studies on hybrid capacitors with metal oxides and activated carbon (AC) as positive and negative electrodes are becoming a matter of major importance in research [9–15]. One of the main reasons is that when using electrolyte containing  $\text{Li}^+$  the charge storage mechanism of some metal oxide electrodes was suggested to be associated with a reversible insertion/extraction of  $\text{Li}^+$  ions in the oxide structure, accompanied by charge transfer at the electrode/electrolyte interface, providing a considerable pseudocapacitance contribution [16–19]. Hence, EDLCs with e.g. an aqueous lithium hydroxide electrolyte have become today a crucial research trend, though the literature data on aqueous LiOH as an electrolyte for capacitors or hybrid capacitors are scanty; only a limited number of reports on the use of lithium hydroxide electrolyte may be found in the available literature [20–22].

In this study we propose a novel EDLC with modified electrode and separator materials and lithium hydroxide as electrolyte. AC cloths and microporous polypropylene (PP) separators were modified with lithiated acetone oligomers created in an aldol condensation process of acetone and a saturated aqueous LiOH solution. The modifier used changed the inherent hydrophobicity of AC and PP materials to the hydrophilic character and made them wettable by an aqueous electrolyte. The EDLC with an aqueous KOH electrolyte is also reported for comparison.

\* Corresponding author. Tel.: +48 616652317; fax: +48 616652571.  
E-mail address: [izabela.stepniak@put.poznan.pl](mailto:izabela.stepniak@put.poznan.pl) (I. Stepniak).

## 2. Experimental

In this study, microporous PP membranes (Celgard 2500, Dai- cel Chemical Industries, Ltd.) were used for experimental EDLCs as separators. Modification of PP pieces was carried out according to the following steps. At first, virgin PP samples were soaked with acetone at 20 °C for 15 min. Successively saturated samples were placed into a 50 ml flask containing a saturated aqueous LiOH solution. After 24 h membranes became hydrophilic and were ready to be used. This two-part procedure with chemistry of modification is presented in the following scheme:



Acetone aldol condensation products (amphiphilic substrates) are created by a chemical reaction taking place in the pores of virgin PP, which may be treated as paint generation that will cover all its

structure. It is important to note that acetone disappears from the membrane structure after the process in question and the produced membrane is hydrophilic and filled with the used LiOH solution. Activated carbon cloths (Kynol® Europa GmbH, No ACC) with a specific surface area of ca. 2000 m<sup>2</sup> g<sup>-1</sup> were modified in the same manner.

After assembling the capacitor by contacting three “foils” (two modified electrodes separated by the modified PP membrane, all filled with saturated aqueous lithium electrolyte), and placing it into the test vessel (Swagelok® system with stainless steel collectors) it was left at a temperature of ca. 50 °C in order to reach the equilibrium between the electrodes and the electro- lyte. The final thickness of the tested capacitor was ca. 0.8 mm. Devices with KOH aqueous solution as the electrolyte were assembled in the same manner, but AC and PP components were modified in the aldol condensation process of acetone and aque-

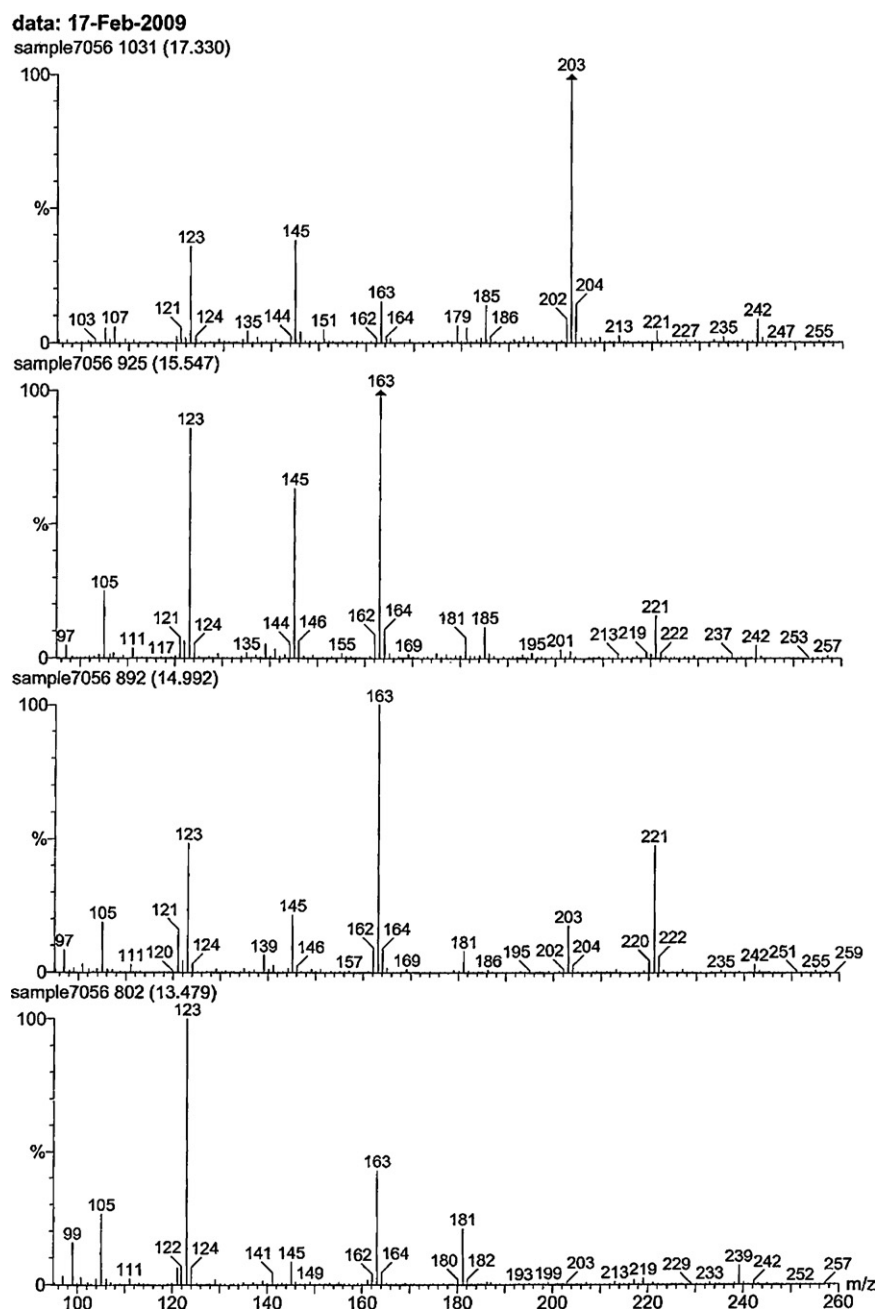


Fig. 1. Mass spectra of the acetone phase after 1 day of contact with saturated LiOH solution.

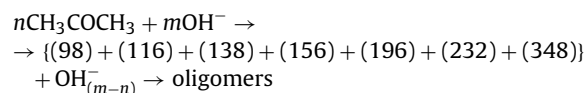
ous KOH solution ( $d = 128 \text{ g cm}^{-1}$ ) as presented in our previous paper [23].

Performances of capacitors were characterized using cyclic voltammetry (CV), the galvanostatic charge–discharge test and the electrochemical impedance spectroscopic method (EIS). CVs (scan rate  $10 \text{ mV s}^{-1}$ ) were performed using a potentiostat/galvanostat system ( $\mu\text{AutoLab FRA2}$  type III, EcoChemie, Netherlands). The charge–discharge characteristics were carried out using the Atlas 0461 MBI multichannel electrochemical system (Atlas-Solich, Poland). EIS measurements, over the frequency range from 0.01 Hz to 99 kHz and the potential amplitude of 10 mV, were taken using the  $\mu\text{AutoLab FRA2}$  type III electrochemical system (EcoChemie, Netherlands). All tests were conducted under ambient conditions.

The process of aldol condensation of acetone with saturated aqueous lithium hydroxide was monitored by HPLC–ES–MS using a Waters Alliance 2690 HPLC. IR spectra ranging from 4000 to  $400 \text{ cm}^{-1}$  of virgin and modified membranes were recorded using a Bruker Equinox 55 FT-IR spectroscope.

### 3. Results and discussion

The submersion of the acetone filled PP membrane (or AC cloth) into a saturated aqueous LiOH solution initiates the aldol condensation process of acetone. It takes place in the closed space, i.e. in the structure of the membrane (or AC cloth). This process was observed using HPLC–ES–MS in a separate experiment, where two immiscible liquids, i.e. acetone and an LiOH solution, were in physical contact. Fig. 1 shows a detailed picture of the process in question; the presented mass spectra were recorded for acetone 1 day after contact of the above mentioned phases. This picture presents only the representative mass spectra from a series of recorded measurements. The collected data show that in mass spectra of the acetone phase after contact with a LiOH solution the highest ion signal intensity was seen for  $[\text{M}+\text{Li}]^+$  ions at  $m/z$  (105), (123), (145), (163), (203), (239) and (355). It means that the main products of the monitored process are mesityl oxide (98), isomesityl oxide (98), mesitylene (116), phorone (138), isophorone (138), semiphorone (156), and unknown products (196), (232) and (348); these findings are in good agreement with the literature data concerning the aldol condensation process of acetone in basic media [24–26]. In compliance with the obtained results the chemistry of aldol condensation of acetone under the examined conditions may be presented as follows:



After the above modification, products of aldol condensation of acetone were anchored on all surfaces of PP or AC substrates, which may be confirmed by FT-IR spectroscopy. Fig. 2 demonstrates examples of IR spectra of virgin PP and modified PP samples; virgin PP samples exhibited several peaks, which are well matched to those reported in the handbook [27]. It can be seen from this figure that there is an absorption peak around  $1700 \text{ cm}^{-1}$  in the spectra of the modified samples, which cannot be observed for the virgin PP sample. This peak is assigned to the stretch of the C=O group. This finding confirms the accumulation of aldol condensation products of acetone in modified substrates, which changes their hydrophobic character to hydrophilic and makes them compatible to aqueous electrolytes.

Fig. 3a shows CVs for tested EDLCs in a 4.6 M LiOH and a 6.7 M KOH aqueous solutions. The CV profiles of both aqueous electrolyte-based capacitors were nearly rectangular in shape (without visible peaks due to redox reactions), suggesting good capacitive devices in both cases. Moreover, good electric contacts at the electrode/electrolyte interface and good compatibility of all

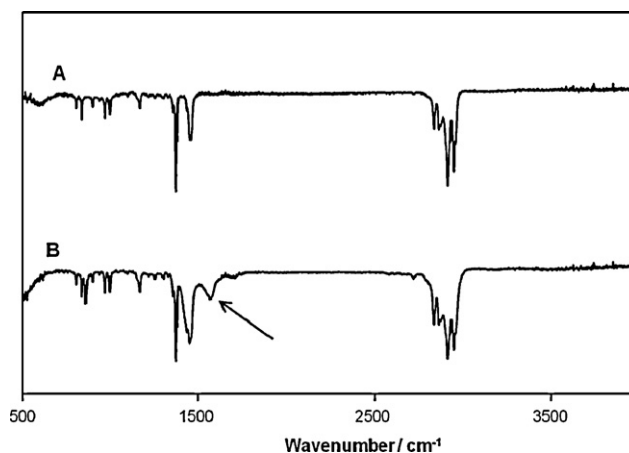


Fig. 2. FT-IR spectra of the virgin PP membrane (A) and modified PP membrane (B).

constituents of the unit capacitor are responsible for good electrochemical characteristics in the EDLC cell with the lithium hydroxide electrolyte, comparable to those with the KOH aqueous solution. From the voltammograms, specific capacitances of the electrodes in the LiOH electrolyte and the KOH aqueous solution were evaluated to be 102 and  $95 \text{ F g}^{-1}$ , which are very close.

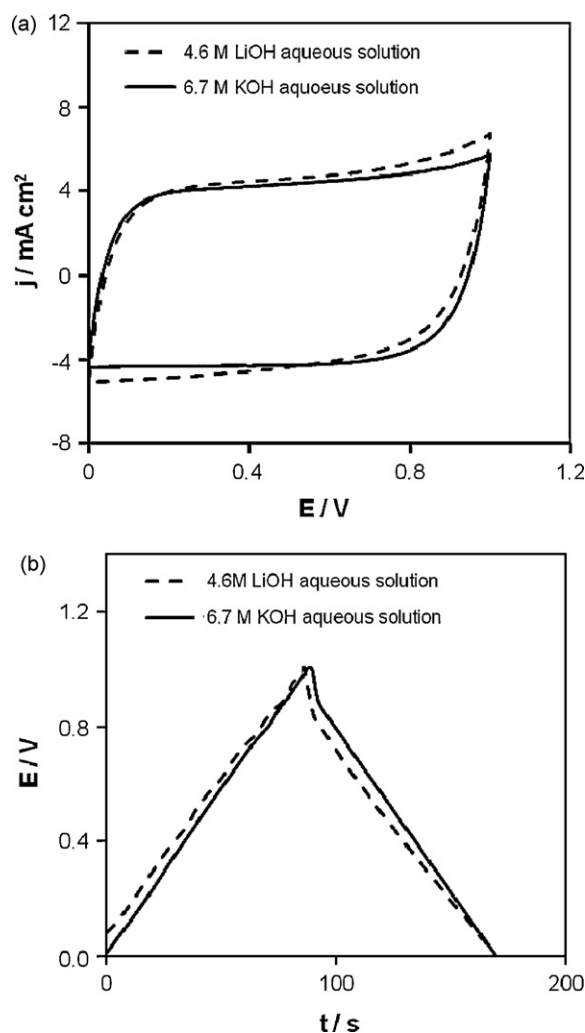


Fig. 3. (a) Cyclic voltammograms for modified EDLC cells with 4.6 M LiOH and 6.7 M KOH aqueous solutions. Scan rate  $10 \text{ mV s}^{-1}$ . (b) Charge–discharge curves (10th cycle) for EDLC cells with 4.6 M LiOH and 6.7 M KOH aqueous solutions. Current density  $5 \text{ mA cm}^{-2}$ .

**Table 1**  
Characteristics of tested EDLCs.

	$C$ [ $F g^{-1}$ ]	$E_{max}$ [ $kJ kg^{-1}$ ]	$P_{max}$ [ $kW kg^{-1}$ ]
EDLC with aqueous KOH	95 <sup>a</sup> , 97 <sup>b</sup> , 90 <sup>c</sup>	24 <sup>a</sup>	14 <sup>c</sup>
EDLC with aqueous LiOH	102 <sup>a</sup> , 108 <sup>b</sup> , 92 <sup>c</sup>	26 <sup>a</sup>	20 <sup>c</sup>

$C$ , specific capacitance;  $E_{max}$ , maximum energy stored and  $P_{max}$ , maximum power.

<sup>a</sup> Calculated from CV.

<sup>b</sup> Galvanostatic measurements.

<sup>c</sup> EIS measurements.

A galvanostatic charge–discharge curves for the experimental EDLC cells with a 4.6 M LiOH solution and a 6.7 M KOH electrolyte are shown in Fig. 3b. Linear curves were observed in each case. This type of capacitive behaviour, with the square shape of voltammograms, confirms good synergy between all phases in the cell. Cell capacitance is deduced from the slope of the discharge curve with:

$$C = \frac{I}{dV/dt} \quad (1)$$

where  $C$  is cell capacitance in farads (F),  $I$  the discharge current in amperes (A) and  $dV/dt$  the slope of the discharge curve in volts per second ( $V s^{-1}$ ). In a symmetrical system, where the active material weight is the same for the two electrodes, specific capacitance  $C_{spec}$  in farads per gram of active material ( $F g^{-1}$ ) is related to the capacitance of cell  $C$  by:

$$C_{spec} = \frac{2C}{m_{el}} \quad (2)$$

where  $m_{el}$  is the weight (g) per electrode of active material.

From the galvanostatic charge–discharge curves, at a current load of  $\pm 5$  mA, specific capacitances of the electrodes were evaluated to be 108 and  $97 F g^{-1}$  for the LiOH and the KOH aqueous electrolytes, respectively, and very close to those based on the CVs. Maximum specific energy ( $E_{max}$ ) and power ( $P_{max}$ ) can also be estimated from this plot (Fig. 3b), using equations:

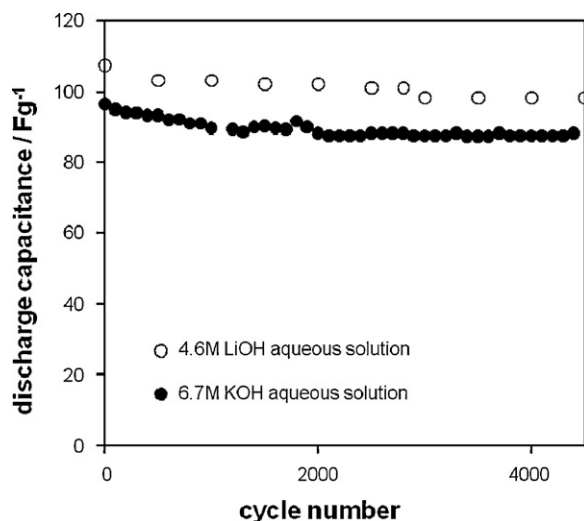
$$E_{max} = \frac{CV^2}{2m_{el}} \quad (3)$$

$$P_{max} = \frac{V^2}{4Rm_{el}} \quad (4)$$

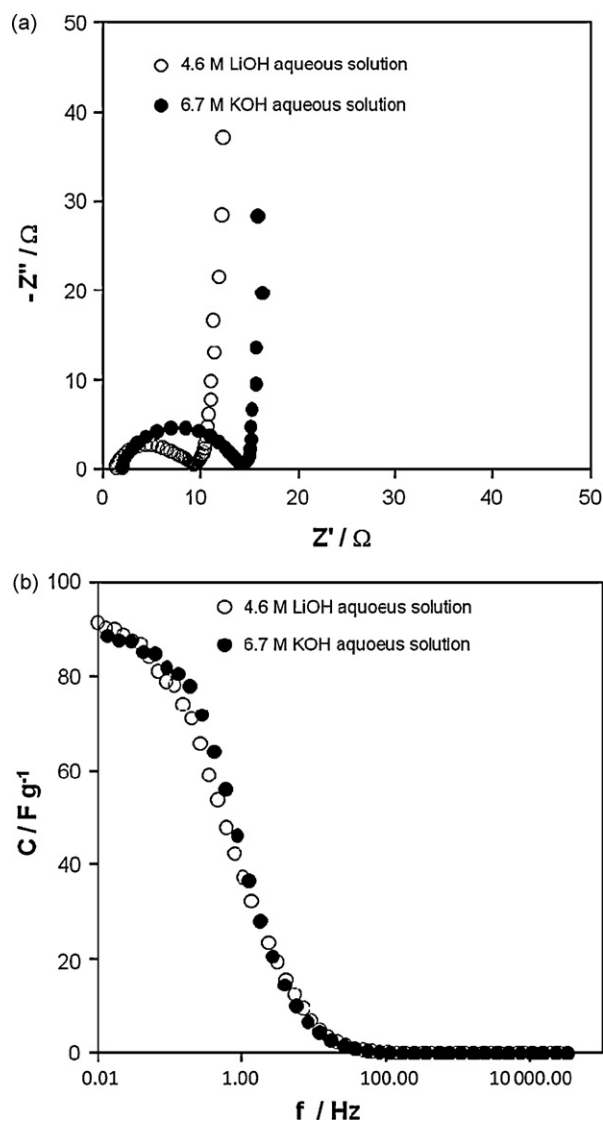
where  $V$  is the operating voltage and  $R$  internal resistance of the capacitor. Calculations are presented in Table 1.

Fig. 4 shows specific capacitance as a function of cycle number for tested EDLC cells using both aqueous solutions. With an increasing cycle number, capacitance of the electrode in the LiOH electrolyte hardly changed, remaining slightly higher than that of the KOH aqueous solution. This suggests that the LiOH electrolyte as well as the KOH aqueous solution are stable under these charge–discharge conditions and, moreover, keep good intimate contact with the modified carbon electrodes.

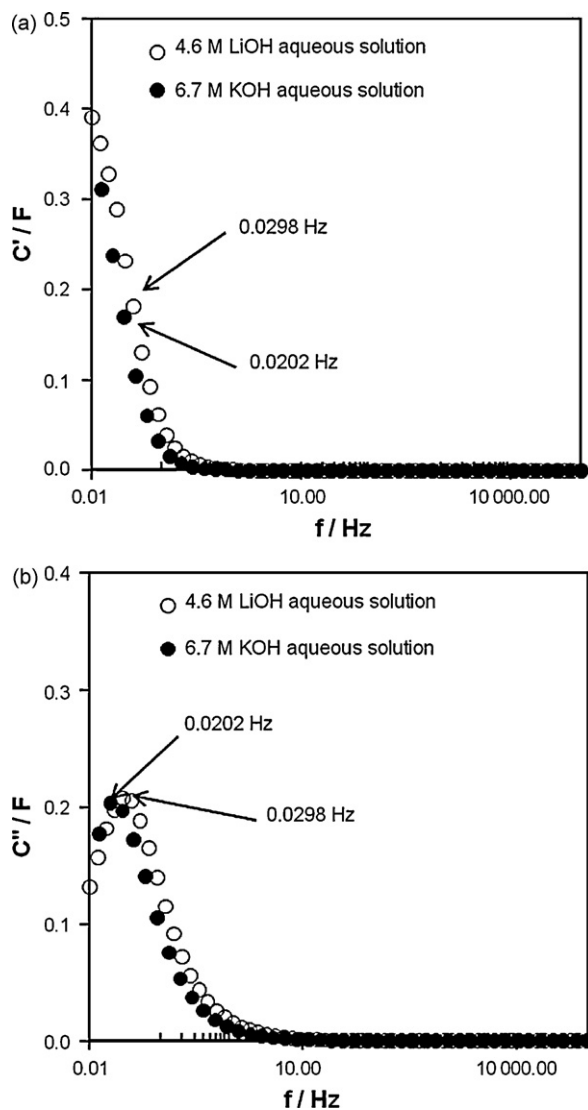
EIS, as a powerful technique for the investigation of capacitive behavior of electrochemical cells, has also been used to check the ability of the novel EDLC design to store electrical energy. An example of Nyquist plots for the capacitor with a LiOH aqueous electrolyte and a KOH solution (both with modified electrodes and a modified separator) are shown in Fig. 5a. In the high-frequency region of each spectrum there appears a single semicircle. From the point of intersecting with the real axis in the range of high frequency, resistance of the cell was estimated to be  $1.3 \Omega$  for the lithium hydroxide electrolyte under these experimental conditions, which is very similar to that for the KOH aqueous solution, i.e.  $1.8 \Omega$ . Following the semicircle with decreasing frequency, the plots are transformed to a vertical line. A line close to  $90^\circ$  attributed to a capacitive behavior was observed for both cases; at higher



**Fig. 4.** Discharge capacitance as a function of cycle number for modified EDLC cells with 4.6 M LiOH and 6.7 M KOH aqueous solutions.



**Fig. 5.** (a) Nyquist plots for modified EDLC cells with 4.6 M LiOH and 6.7 M KOH aqueous solutions. (b) Specific capacitances vs. frequency plot obtained from EIS for tested EDLCs.



**Fig. 6.** (a) Variation of the real part of capacitance with frequency for EDLC cells with 4.6 M LiOH and 6.7 M KOH aqueous solutions. (b) Variation of the imaginary part of capacitance with frequency for EDLC cells with 4.6 M LiOH and 6.7 M KOH aqueous solution.

frequencies, the capacitor behaves like a pure resistor and at low frequencies shows capacitive behavior [28]. Specific capacitances of tested devices calculated from the imaginary part of the complex impedance spectrum:  $C = (2\pi f Z'' )^{-1}$ , and plotted as functions of frequency are shown in Fig. 5b (obtained values at 0.01 Hz are identical to those calculated from CVs and charge–discharge tests, i.e. 90 and 92  $\text{F g}^{-1}$ ). Capacitance is high at low frequencies, for both cases, and starts to decrease at higher frequencies of around 0.1–10 Hz. This region corresponds to the transition between semicircle and the straight line in Fig. 5a.

Fig. 6 a and b presents a simple way to model the capacitor frequency behavior by using impedance data, by analogy with the study published earlier [29,30]; this model shows relationships between  $C'(\omega)$ —the real part of capacitance  $C(\omega)$  with  $Z''(\omega)$  and  $C''(\omega)$ —the imaginary part of capacitance  $C(\omega)$  with  $Z'(\omega)$ :

$$C'(\omega) = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2} \quad (5)$$

$$C''(\omega) = \frac{Z'(\omega)}{\omega |Z(\omega)|^2} \quad (6)$$

$C'(\omega)$  corresponds to the capacitance of the cell that is measured during constant current discharge (direct current), and  $C''(\omega)$  corresponds to losses in the form of energy dissipation.

Fig. 6 a and b presents variation of the real and the imaginary parts of capacitance with the frequency for capacitors based on an aqueous LiOH solution or a KOH electrolyte. Fig. 6a shows the relationship between  $C'$  and frequency. At a low frequency (10 mHz), the capacitance of the electrode has reached 0.39 F for the device with an aqueous LiOH solution and 0.33 F for the KOH electrolyte. This low frequency capacitance ( $C_{LF}$ ) corresponds to the cell capacitance measured during galvanostatic cycling at  $\pm 5$  mA. When frequency is increased, capacitance decreases, and at a high frequency the capacitor behaves like a pure resistor. Fig. 6b shows the relationship between  $C''$  and frequency for the tested devices;  $C''$  passes through a maximum at 20 mHz for the former and 30 mHz for the latter. From this figure it is possible to deduce the relaxation time constant that defines the frontier between capacitive behavior and resistive behavior of the capacitor. The relaxation time is deduced from frequency  $f_0$  with  $\tau_0 = 1/f_0$ ;  $f_0$  may be obtained from the real capacitance plot at  $C' = C_{LF}/2$  and from the imaginary capacitance plot, where it corresponds to peak frequency.

Time constants are very different, as seen in Fig. 6b 49.5 and 33.5 s, respectively, when using an aqueous KOH solution and LiOH solution as a capacitor electrolyte. The capacitor using LiOH is able to deliver its stored energy faster than the capacitor with the KOH electrolyte, i.e. at higher power. This is probably connected with the difference in viscosities between the two solvents, leading to a difference in the electrolyte penetrations inside the porous structure of the electrode material. Best results are then obtained with the lithium hydroxide electrolyte.

Electrochemical properties of tested devices calculated from cyclic voltammetry, galvanostatic charging–discharging and impedance spectroscopy are shown in Table 1. Presented data provide valuable information to explore the novel composition of EDLC with an aqueous LiOH electrolyte.

#### 4. Conclusion

The new design of EDLCs was tested with saturated aqueous lithium hydroxide used as an electrolyte. The devices were assembled using thin polypropylene separators and activated carbon cloths, both modified with lithiated acetone oligomers as a product of aldol condensation process of acetone and a saturated aqueous LiOH solution. In cyclic voltammetry and charge–discharge cycle tests, the EDLC cells showed a similar capacitive behavior to that for a KOH aqueous solution, but showed higher power. This indicates that tested devices with a good and stable electric contact at the electrode/electrolyte interface could be constructed using the LiOH aqueous solution as an electrolyte. Presented electrochemical characteristics clearly indicate that the new design of the cell with an intimate contact of all components, owing to the modifying layer, has a potential applicability to EDLCs from the practical point of view.

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