

Green Alternative binders for high-voltage electrochemical capacitors

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Abstract. Different polymer binders have been studied for applications in positive and negative electrodes of lithium-ion capacitor (LIC). The current work describes also some new approaches for changing the electrode fabrication process from organic to aqueous solvents in order to reduce the cost of the electrode making process. LIC electrodes made from Solef[®] PVDF aqueous dispersions have revealed a superior electrode quality and a high electrochemical performance. These achievements have demonstrated the possibility to develop an environmentally friendly production process of LIC.

1. Introduction

An electrochemical device would best fit for the automotive technology once the compromise between specific energy and power density is established. Even though Li-ion batteries (LIB) are famous storage technologies representing the highest energy densities, and can now be designed to deliver also a high power, some important drawbacks such as limited cycle life and safety problems give rise to important concerns for their widespread use, particularly in transport area. On the other hand, carbon-carbon electric double layer capacitors (EDLC) have relatively unlimited cycle-life, very high specific power but not enough energy densities. A new type of nonaqueous hybrid device, also known as lithium ion capacitors (LIC), was first introduced by Amatucci et al.[1] This hybrid system basically combines a battery negative electrode and an EDLC type positive electrode to profit the advantages of both technologies [2].

Despite several factors impacting LIC power and energy densities, electrode manufacturing parameters merit special attention to reach the best performance. In this sense selection of binder is one of the crucial steps of electrode manufacturing. A high performance binder should establish a high adhesion of the electrode active materials to the current collector along with the ability to form a good electric network between the active material and conductive carbon in order to improve both the electron transport and the diffusion of the lithium ion. Optimization of the different binder systems for electrode fabrication is one of the ways to develop high performance electrochemical storage devices.



Among different polymer binders, poly(vinylidene fluoride) (PVDF) have been widely applied as binder due to their excellent chemical, thermal and electrochemical stability [3]. Nevertheless, their main shortcoming is the organic solvent which is generally used to achieve the complete dissolution of PVDF in order to provide a good adhesion. Currently, the common organic solvent for preparation of the electrode slurry is N-methyl-2-pyrrolidone (NMP).

Recent approaches have been devoted to avoid hazardous organic solvents and to replace them with more environmentally friendly alternatives. Aqueous-based solutions have been proposed to develop a greener process for electrode manufacturing. The use of organic solvents is avoided and replaced by water as solvent media. A lot of efforts had been put into practice to search for alternative water-based binders and to improve the electrochemical performance. Carboxymethyl cellulose (CMC) [4,5], polyacrylic acid (PAA) [6,7] and polyvinyl alcohol (PVA) [8,9] have been extensively tested. The system based on Styrene-Butadiene Rubber (SBR) and CMC is the most studied water-based binary binder combination.

In this study a pioneering slurry concept targeting the use of an environmentally benign slurry solvent and aqueous-based binder systems were investigated for constructing LIC electrodes. For this purpose Solef® PVDF aqueous dispersions were successfully employed as novel binders for LIC's electrodes. Both adhesion and electrochemical performance evaluation in coin cells were realized and compared to NMP-based electrode development. As a consequence of the utmost efforts to change the binder type from organic to aqueous. Solef® PVDF aqueous dispersions alternatives were employed as binders due to desired electrochemical and chemical stability. LIC electrodes are manufactured, and complete electrochemical tests were performed in comparison to the well-established CMC-SBR system.

2. Experimental

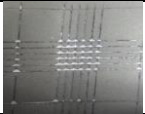
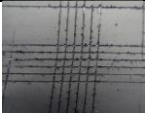
In this work, versatile electro-chemical testing has been conducted with different active materials in order to estimate their possible application for lithium-ion capacitors. Electrodes were composed of 80-91% of active materials (graphite or activated carbon) type, 5-10% of the binder, and 1-5% of carbon percolators. In current work activated carbon YP 50-F from Kuraray Co. selected for the positive electrodes of LIC. SLK1520P graphite sample from Superior Graphite Co had been selected for the positive electrodes of LIC. The carbon C65 from Timcal was used as a percolator for negative and positive electrodes. Slurries for electrode casting were prepared from a mixture of the active materials and solutions of binder. Tape casting with 100 μm gap was carried out by "Doctor blade" method. Dry electrodes, with a thickness within the range of 20-80 μm , were calendared by Hot Rolling Machine from MTI. Then electrodes were cut by the MTI disk cutter into 15 mm circular samples. Later the samples further dried at 120°C and transferred to the argon filled MBraun glove box for storage until cell assembling took place. The electrochemical tests carried out using a coin-type cell (CR-2025 from MTI). The electrochemical performance of materials is examined using different measurement techniques. Electrochemical investigations were performed using the multi-channel potentiostat/galvanostat VMP3 from Princeton Applied Research (UK).

3. Results and Discussion

The composite electrodes need to have enough mechanical stability, including good adhesion of the active materials to the substrate and high adhesion between the particles of active materials to get the best electrochemical performance. This is because much attention dedicated to explore the material adhesion to the current collector by varying electrode's composition and binders and electrode processing. Adhesion has been measured by peeling test following ASTM D 3359. In the current work electrodes of LIC are prepared from slurries based on activated carbon and different binders. Also, we tested electrodes made from slurries containing different solvents such as NMP or water. In this investigation, we clarified affects which influenced on the adhesion of active materials.

The table 1 shows the summarized results of adhesion tests applied on electrodes made according to different conditions. The results lead to a conclusion that applying the proper processing conditions, electrodes which made using water based binder show the same adhesion level electrodes based on PVDF polymer processed in NMP. Thus, replacing of NMP by water-based binders is a major step towards realizing an environmentally friendly, cost efficient and safer method of electrode development.

Table 1. The summary results of adhesion tests for electrodes with different binder materials

Composition of electrodes (%, w/w)	Electrode surface of cross-cut area from which flaking has occurred		Conclusion
	After incisions	After removing tape	
Activated Carbon (YP-50F)- 90 %, C65-5%, PVDF (NMP)-5%			Bad adhesion
Activated Carbon (YP-50F)- 85 %, C65-5%, PVDF (NMP)-10%			Good adhesion
Activated Carbon (YP-50F)- 89 %, C65-5%, CMC-2%, SBR-4%			Good adhesion
Activated Carbon (YP-50F)- 89 %, C65-5%, CMC-2%, PVDF Latex-4%			Good adhesion
Graphite (SLK1520P)-92%, C65-1%, PVDF (NMP)-7			Good adhesion
Graphite (SLK1520P)-93%, C65-1%, CMC-3%, PVDF Latex-3 %			Good adhesion

3.1. Electrochemical performance of positive electrode

The internal resistance is the key parameter for determining power, energy efficiency of a supercapacitor. In this work the internal resistance of supercapacitor has been determined by Electrochemical Impedance Spectroscopy (EIS) techniques. As Fig.1 shows the internal resistance of supercapacitor can be easily obtained from Nyquist plot. The internal resistance can be specified as Equivalent Series Resistance (ESR) and Equivalent Distributed Resistance (EDR). ESR is the resistance due to all the resistive components within the supercapacitor. The EDR resistance includes the ESR resistance and an additional contribution from the charge redistribution process in the electrode.

In this work, water-based binders were employed as an alternative slurry solvent instead of NMP. Fig. 2 shows Nyquist plots of the EDLC cells assembled with activated carbon (AC) electrodes based on different binders. Fig. 10 shows Nyquist plots of the EDLC cells assembled with AC electrodes based on different water based binder. Comparing the results in table 2 leads to the conclusion that AC electrodes, made from a water-based binder, show better electrochemical performance as standard

PVDF processed in NMP. Thus, according to our results, the proposed techniques should be potential alternatives to a common fabrication process of lithium-ion capacitor electrodes based on NMP.

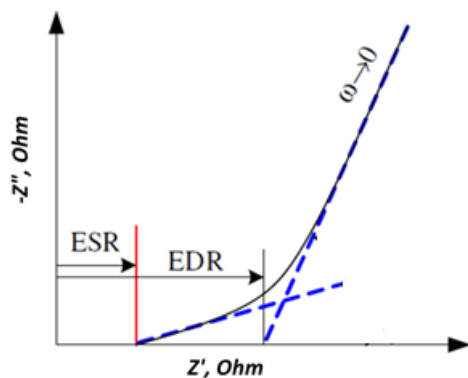


Figure 1. Determination of ESR and EDR from Nyquist plot

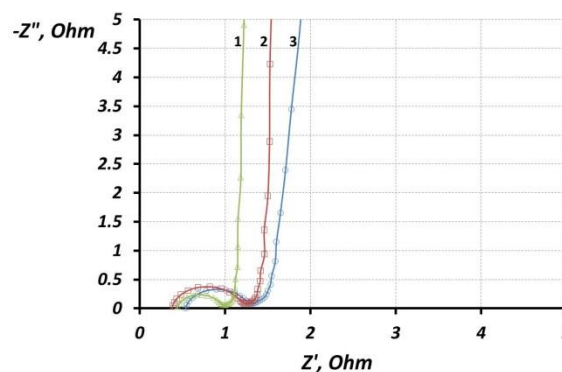


Figure 2. Nyquist plots of the EDLC cells assembled with AC electrodes based on different water based binder:

- 1- CMC-PVDF Latex
- 2- PVDF processed in NMP
- 3- CMC-SBR

Table 2. The summary results of electrochemical tests for EDLC capacitor based on electrodes with different binder materials

Composition of electrodes (%, w/w)	R_{ESR}, Ohm	R_{EDR}, Ohm
YP-50F-89 %, C65-5%, CMC-2, SBR-4%	0.51	1.53
YP-50F-89 %, C65-5%, CMC-2%, PVDF latex -4 %	0.44	1.15
YP-50F-89 %, PVDF (NMP)	0.71	1.45

3.2. Electrochemical performance of negative electrode

The electrochemical investigation of all anodes was started with the first lithiation performed against metallic lithium. Fig. 3 shows the initial charge/discharge curves of the SLK1520P graphite electrode which was prepared using the standard method with NMP as solvent for electrode slurry. The table 3 sums up initial charge/discharge performance for the SLK1520P graphite samples from Superior Graphite Co. The difference between the specific charge of the first lithiation, and the reversible specific charge (Q_{rev}) of the following de-lithiation is defined as the irreversible capacity loss of the graphite electrode. The irreversible capacity loss (Q_{irr}) is a measure of the capacity lost due to SEI formation on graphite anode. The reversible capacity of SLC1520P graphite at the first cycle was of $Q \sim 358 \text{ mA}\cdot\text{h/g}$; this is quite close to the theoretical capacity. Irreversible loss of capacity at the first cycle came to $18 \text{ mA}\cdot\text{h/g}$ ($\Delta \sim 5 \%$). The above-mentioned grade of graphite has been selected for LIC due to their lowest irreversible capacity. The same test was done for electrodes with different binders. Results of investigation are included in Table 3 as well. It seems that electrodes made with aqueous binders show the same electrochemical performance as standard PVDF processed in NMP.

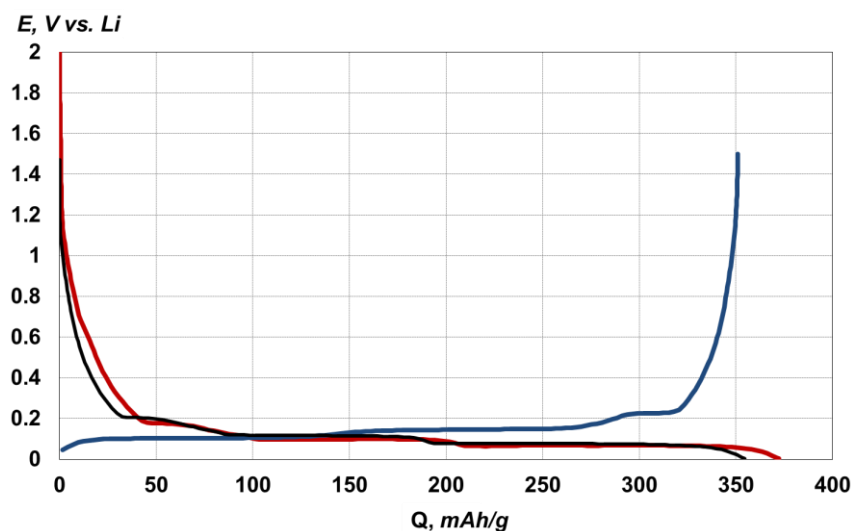


Figure 3. Charge and discharge profile of the half - element based on the reference SLC1520P graphite at the current density C/10.

Table 3. Electrochemical performance of anode based on different binder materials

Anode composition	Q_{rev} , $mA \cdot h/g$	Q_{irr} , $mA \cdot h/g$
SLK1520P -91%, C65-1%, PVDF(NMP)-8%	358	18
SLK1520P -93%, C65-1%, CMC-3%, PVDF Latex-3%	362	17
SLK1520P -93%, C65-1%, CMC-3%, SBR-3%	356	23

The electrodes based on aqueous binders are very promising in terms of electrochemical performances of the negative electrode. In combination with the advantage of enabling usage of water as solvent for the electrode preparation process, these electrodes certainly deserve further investigation and optimization efforts.

3.3. Electrochemical performance of lithium-ion capacitor

The electrochemical performances of the lithium ion capacitors were investigated. LICs were assembled with pre-lithiated graphite anode and AC cathode based on aqueous binder. Fig. 3 and 4 show the charge-discharge curves of LIC based on water-based binder with a potential range of 2.0-4.5 V at a current density of 1C.

The Ragone plots are illustrated in Fig. 4, which were obtained by calculating the energy density and power density at different current densities. It should be noted that both the energy density and power density of LIC based on aqueous binder (CMC- PVDF latex) improved in comparison to LIC with electrodes based on PVDF processed in NMP. Designed LIC with PVDDF latex binder has the maximum energy density of 80 W·h/kg. Also the highest power density (of about 20 k·W/kg) is possible to achieve. Thus advanced LIC show the best combination of energy density and power density, what is especially important for automotive application.

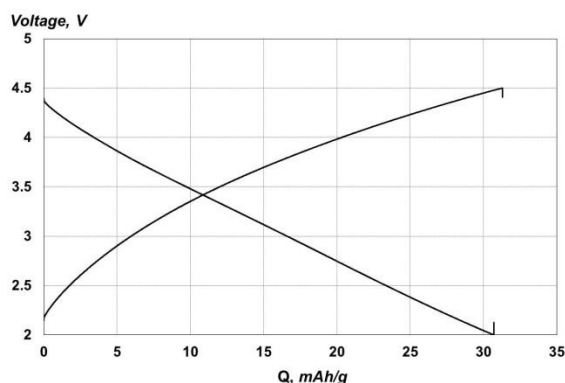


Figure 3. Charge-discharge curves of the LIC assembled with activated Carbon (cathode) and Graphite (anode). Specific capacity calculated per mass of cathode.

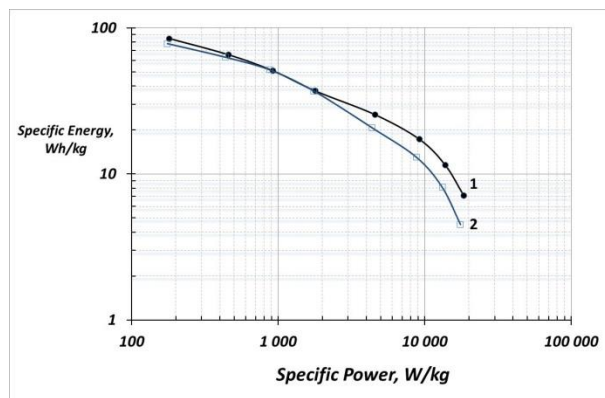


Figure 4. The Ragone plots for the LIC accepted with electrodes using different types of binders:

1-CMC-PVDF Latex

2-PVDF processed in NMP

4. Conclusion

The obtained results enlighten the promising prospect of innovative slurry concept for the fabrication of LIC electrodes. These achievements have demonstrated the possibility to develop LIC environmentally friendly production processes. Applying the proper processing conditions, electrodes made with water-based binders (CMC/SBR, CMC-PVDF Latex) show the similar electrochemical performance as standard PVDF processed in NMP. Through comparing the electrochemical performance different electrodes based on SBR and novel Solvay product such as PVDF latex it can be concluded that PVDF-latex shows better performance than SBR.

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