Tuning Conducting Polymer Dispersions for High-CV Tantalum Capacitors

Udo Merker, Wilfried Lövenich, Klaus Wussow
H.C. Starck GmbH
Central Research & Development
Building B 202
51368 Leverkusen, Germany
phone: ++49-214-3023671
fax: ++49-214-3025973
e-mail: udo.merker@hcstarck.com

Abstract

Polymer electrolyte capacitors are a fast growing segment within the tantalum capacitor market. The superior performance of polymer electrolytes compared to standard manganese electrolytes makes tantalum polymer capacitors the first choice for low equivalent series resistance applications in modern electronic circuits.

New conducting polymer dispersions support the market growth of polymer capacitors by simplifying the manufacturing process dramatically and by enhancing the performance of the capacitors further. Applications that have not been accessible by traditional manufacturing processes so far have been opened up by the use of conducting polymer dispersions. For example polymer electrolyte tantalum capacitors with rated voltages up to 50V are now feasible.

Impregnation of polymer particles into porous tantalum anodes is challenging when very high-CV tantalum powders are used. Very small pore sizes in state of the art powders with a specific capacitance of for example 150.000 µFV/g require improved polymer dispersions. We have tuned conducting polymer dispersions to improve impregnation of high-CV tantalum capacitors.

Introduction

Since the discovery of the electrical conductivity of doped polyacetylene by Shirakawa, MacDiarmid and Heeger in 1977 [1] a variety of conducting polymers and many applications for conducting polymers have been developed (see Fig.1). Today 30 years later solid electrolyte capacitors are the major market for conducting polymers. Conducting polymers form the cathode in polymer electrolyte capacitors. Due to their high electrical conductivity and self-healing property conducting polymers are more and more replacing other solid electrolytes like MnO_2 or TCNQ. The equivalent series resistance (ESR) of solid electrolyte capacitors could be reduced by conducting polymer cathode materials significantly.

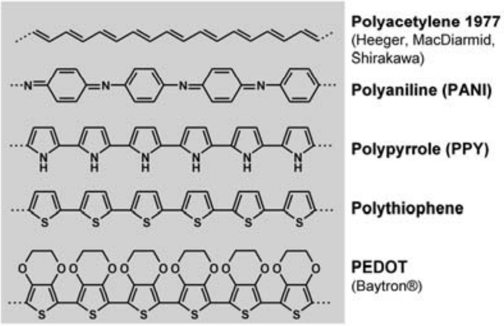

Fig. 1: Most common conducting polymers.

Within the last 30 years the performance of conducting polymers has been enhanced significantly. While the initially developed conducting polymer polyacetylene was too unstable, conducting polypyrroles, polyanilines and polythiophenes were evaluated to manufacture solid electrolyte capacitors. In the early 90th of last century first tantalum and aluminum polymer capacitors were introduced into the market [2,3]. At that time polypyrrole was the material of first choice because it outperformed polyanilines or polythiophenes. Meanwhile a new, highly temperature stable conducting polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), had been developed by Bayer (trade name Baytron®)[4]. In the late 90th first polymer electrolyte capacitors based on PEDOT were commercialized [5]. Soon after PEDOT became the material of first choice. Processing of PEDOT was much simpler than of pyrrole and its temperature stability outreached that of polypyrrole and polyaniline by far. Moreover in 1999 serious health risks for workers handling polypyrrole in capacitor manufacturing had been reported [6]. Today PEDOT has by far the highest market share for conducting polymers in the capacitor market.

Figure 2 shows the manufacturing process for a polymer tantalum capacitor schematically. Highly porous tantalum powder is pressed and sintered to an anode pellet. A Ta_2O_5 dielectric is formed on the surface of the anode pellet by electrochemical anodization. The conducting polymer cathode is made on the dielectric by chemical in-situ polymerization of a monomer by the use of an oxidizer. The polymerization reaction for PEDOT is shown in Figure 3. Fe(III)-salts like Fe(III)-toluenesulfonate are commonly used as oxidizers for the polymerization. Finally the capacitor is contacted and encapsulated.

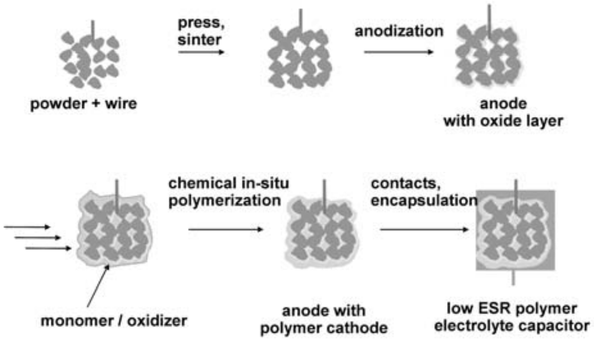

Fig. 2: Manufacturing process of conducting polymer tantalum capacitors.

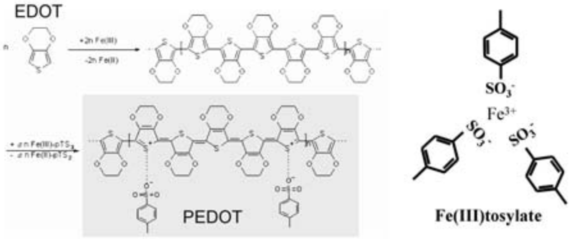

Fig.3: Chemical polymerization reaction of 3,4-ethylenedioxythiophene (EDOT) to poly(3,4.-ehtylendioxythiophene) (PEDOT) using Fe(III)toluenesulfonate as oxidizer

Conducting Polymer Dispersions

The chemical in-situ polymerization for polymer electrolyte capacitors is challenging. A sophisticated process is required to control the polymerization reaction and to achieve a high performance capacitor of low ESR. For tantalum capacitors many polymerization cycles have to be applied. After each cycle remains of the oxidizer and excess of monomer have to be washed out of the porous structure to ensure an efficient next cycle. To overcome these issues with chemical in-situ polymerization and to simplify the manufacturing process we developed nano-scale conducting polymer dispersions for the formation of the cathode layer within the porous structure of electrolytic capacitors [7]. Our polymer dispersions have been introduced to the capacitor market under the trade name Baytron® K-nano successfully.

Baytron® K-nano is a non-hazardous waterborne dispersion of the highly stable conducting polymer PEDOT. The mean size of the conducting particles in the dispersion is about 30 nm. Films made of this dispersion show excellent conductivity of up to 500 S/cm and withstand lead-free reflow temperatures of up to 260°C. A cathode layer within the porous anode structure of the capacitor can be formed by a simple coating and drying process.

The use of our PEDOT polymer dispersion has major advantages against a chemical in-situ polymerization. First of all no polymerization reaction is required. Thus a much faster, more stable and less capital expensive processing is achieved. There are no side products that have to be washed out. Furthermore our polymer dispersion does not deteriorate the quality of the dielectric oxide layer. A chemical in-situ polymerization results in electrical shorts which have to be repaired by additional anodization steps as far as possible. Due to the particle nature of our polymer dispersion defects in the dielectric are not addressed and the quality of the dielectric is not degraded [7]. The deterioration of the dielectric oxide layer by chemical in-situ polymerization is best seen for high voltage polymer capacitors: For example for a tantalum anode which was anodized at 100 V the break-down voltage of the dielectric is degraded to about 45-65 V by a chemical in-situ polymerization. On the contrary our polymer dispersion does not deteriorate the oxide layer and thus a break-down voltage close to the anodization voltage is realized (see Fig. 4).

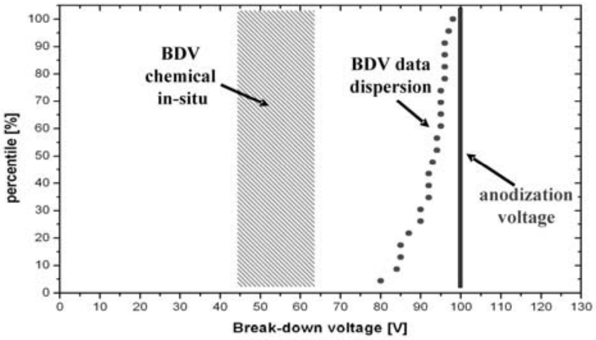

Fig.4: Comparison of break-down voltage (BDV) of polymer tantalum capacitors having polymer cathodes made by chemical in-situ polymerization and by polymer dispersions. Tantalum anodes were anodized at 100 V.

Dispersions for High-CV Tantalum Capacitors

Tantalum powders with a specific capacitance of 150 000 μC/g (150 K) and higher have been developed to meet the market requirements for continuous miniaturization [8]. With increasing specific capacitance the surface of the tantalum powder increases and the average pore size decreases. Capacitor anodes made of such high CV powders are more difficult to impregnate with polymer dispersions than with a chemical reaction mixture due to the particle nature of the polymer.

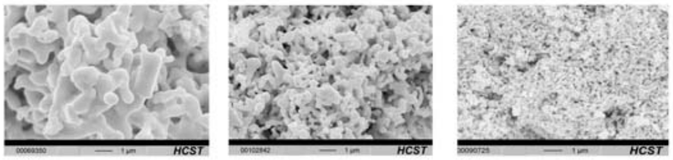

Fig. 5: SEM pictures of primary structure of 18K (left), 50K (center) and 150K (right) tantalum powder anodes

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At the CARTS Europe 2006 conference we reported to achieve similar results on anodes made of tantalum powders up to 70 000 μC/g (70 K) with our polymer dispersion and chemical in-situ polymerization. For a 150 000 μC/g (150K) powder in a small case size anode we were not able to recover more than 35% of the capacitance which we achieved by chemical in-situ polymerization [7].

Meanwhile we were able to synthesize a PEDOT polymer dispersion that has a tighter particle size distribution than our previous dispersion. Figure 6 shows a comparison between particle size distribution of the new and old dispersion. While the average particle size of the new and old dispersion is similar, the new dispersion contains much less larger particles than the old one.

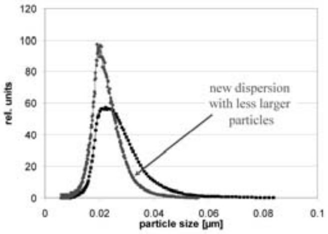

Fig. 6: Particle size distribution of standard and new polymer dispersion.

We have evaluated the performance of our new polymer dispersion in comparison to a chemical in-situ polymerization for various high CV tantalum powders and different anodes sizes. Goal of our experiment was not to achieve polymer capacitors with state of the art performance which would have required sophisticated optimization for each process, powder and anode design. Rather this comparative experiment should give evidence if the impregnation of high CV tantalum powders is hindered by the particle size distribution of the polymer dispersion. If particles are too large for impregnation results for chemical in-situ polymerization where no particles but solutions are applied should be much better.

We have tested our new polymer dispersion on small anodes (P case size) made of tantalum powders with a specific capacitance of 50 000 µC/g (50K), 100 000 µC/g (100K) and 150 000 µC/g (150K). All anodes were anodized to 20 V. For comparison chemical in-situ polymerization was applied to anodes of the same batch [9]. The capacitance and ESR achieved with our new dispersion is listed in Table 1 in relation to the data of the chemical in-situ process. We could achieve about 90% the capacitance that is recovered by the chemical in-situ polymerization. ESR is similar for both processes.

Typically smaller anodes are easier to impregnate than larger anodes. In order to check the impact of anode size on impregnation efficiency we applied our new polymer dispersion and the chemical in-situ polymerization in the same way as before to medium size anodes (low profile B case) which were about 3 times larger than the P case anodes used in the previous experiment. For this experiment we used anodes made of 100 000 µC/g (100K), 150 000 µC/g (150K) and 200 000 µC/g (200K) tantalum powder. Results are shown in Table 2. For this much larger anode size impregnation efficiency for our polymer dispersion is similar to chemical in-situ polymerization as well. Even the impregnation of tantalum powder having an extremely high specific capacitance of 200 000 µC/g seems not be limited by the particle size of the polymer dispersion.

Ta powder [µFV/g]	capacitance dispersion/ chemical [%]	ESR dispersion/ chemical
50 K	92	1.00
100 K	95	0.94
150 K	86	1.09

Tab.1: Comparison of capacitance and ESR achieved with polymer dispersions and chemical in-situ polymerization on P case capacitors made of different high-CV Ta powders.

Ta powder [μFV/g]	capacitance dispersion/ chemical [%]	ESR dispersion/ chemical
100 K	98	0.9
150 K	94	0.9
200 K	87	1.1

Tab.2: Comparison of capacitance and ESR achieved with polymer dispersions and chemical in-situ polymerization in low profile B case capacitors made of different high-CV Ta powders.

Conclusions

Our conducting polymer dispersions offer great potential for the future of solid electrolyte capacitors: The manufacturing process of conducting polymer electrolyte capacitors can be greatly simplified by our dispersions. Furthermore polymer dispersions overcome the problem of dielectric oxide deterioration which is inherent to chemical in-situ polymerization. Thus reliability and voltage range of polymer capacitors can be increased. We have developed a new conducting polymer dispersion with a narrower particle size distribution based on highly temperature stable PEDOT. Our dispersion shows an improved impregnation efficiency which is comparable to a chemical in-situ polymerization for capacitor anodes made of tantalum powder with a specific capacitance of up to 200 000 μC/g. Thus the size of the particles in the new dispersion does not limit the impregnation any more. Although the manufacturing of such high-CV tantalum capacitors using polymer dispersions will require much more work on the material as well the processing to realize state of the art performance the high potential of polymer dispersion could be demonstrated clearly.

References

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