

Conducting Polymer Dispersions for High-Capacitance Tantalum Capacitors

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Abstract

Conducting polymers used as cathode material are the key component in electrolytic capacitors to meet the market needs for low equivalent series resistances (ESR). While polymer electrolyte capacitors have gained substantial market share in the last years, complicated manufacturing processes limit a faster market penetration.

So far conducting polymers are deposited in situ to form the cathode layer either by chemical polymerization or electrochemical polymerization. We have developed conducting polymer dispersions based on our Baytron[®] technology which allow for the direct deposition of the cathode layer by a simple coating process without any polymerization. Unlike polymerization processes the coating with our polymer dispersions does not degrade the dielectric oxide layer. Thus the leakage current and break-down voltage of the dielectric is not deteriorated.

The use of our polymer dispersions for low-capacitance tantalum anodes could be demonstrated. With increasing surface area of the anodes the deposition of conducting polymer dispersions gets challenging due to the decreasing pore sizes. We have developed dispersions as well as deposition processes for high-surface tantalum anodes. In our presentation we will compare the performance of conducting polymer dispersions and chemical polymerization processes for anodes made of various high-capacitance tantalum powders.

Introduction

Polymer electrolyte capacitors are premium products in today's electrolytic capacitor market: Most of the market growth and the profit is attributed to polymer electrolyte capacitors. The performance of polymer electrolyte capacitors has been improved significantly over the last years. Today their ESR performance outreaches that of traditional solid electrolytic capacitors by far.

A faster market penetration of polymer electrolyte capacitors is hindered by sophisticated manufacturing processes: The conducting polymer cathode is polymerized in situ within each single capacitor either by a chemical polymerization or an electrochemical process. The control of chemical reactions within millions of small capacitor anodes is not an easy task,

especially when many process steps are involved. Side products of the polymerization have to be removed to guarantee a stable performance over the life time of the capacitor. Usually the process window for polymerization is very tight to ensure a high yield and constant quality. Thus the scale-up of production lines for polymer electrolyte capacitors can be very challenging and expensive.

Furthermore the application of polymer capacitors is limited to voltages up to about 20V. This limitation is due to the degradation of the dielectric oxide layer of the capacitor anode during the polymerization process. While for low voltages the quality of dielectric oxide layer can be restored by a reformation process, for higher voltages the restoration typically fails. For a further market penetration high voltage applications of polymer electrolyte capacitors have to be addressed.

Conducting Polymer Dispersions for Electrolytic Capacitors

High performance conducting polymers are not soluble. Therefore in-situ polymerization has to be applied for the formation of a conducting polymer cathode in electrolytic capacitors so far. We developed conducting polymer dispersions based on

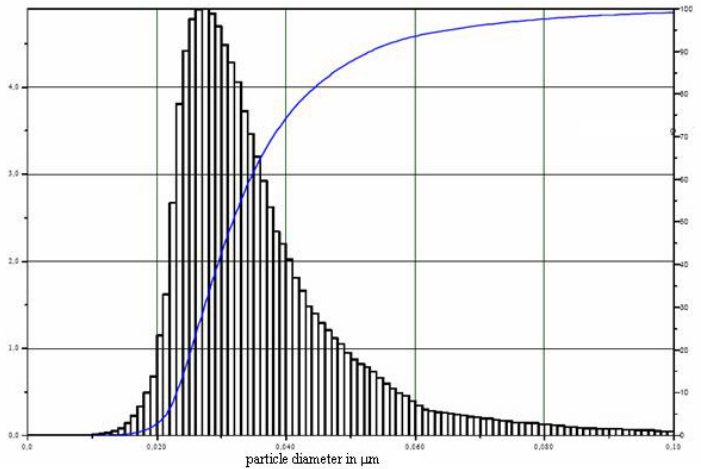


Fig.1: Particle size distribution of conducting polymer dispersion

poly(3,4-ethylenedioxythiophene) which simplify the manufacturing process of polymer capacitors [1]. These dispersions do not penetrate the porous anode structure but are used for the formation of the outer polymer layer on capacitor anodes. The manufacturing of polymer electrolyte capacitors is facilitated significantly by these conducting polymer dispersions because all process steps of the chemical or electrochemical polymerization which are applied for the outer polymer layer formation can be substituted by a simple coating step.

To further simplify the manufacturing process and to replace the in-situ polymerization completely we have developed nano-scale conducting polymer dispersions for the formation of the cathode layer within the porous structure of electrolytic capacitors. This cathode layer formation is much more challenging than the built-up of the outer polymer layer: the

electrical conductivity of the dispersion has to be very high and the dispersion must be capable to impregnate highly porous anode structures.

Our newly developed dispersion is a waterborne dispersion of the conducting polymer poly(3,4-ethylenedioxythiophene). The mean size of the conducting particles in the dispersion is about 30 nm (see figure 1). Films made of this dispersion show excellent conductivity of up to 500 S/cm. A cathode layer within the porous anode structure of the capacitor can be formed by a simple coating and drying process (see figure 2). Since no polymerization is applied the manufacturing process is very robust. Furthermore our new polymer dispersion does not deteriorate the quality of the dielectric oxide layer. Thus there is no need for a reformation of the dielectric.

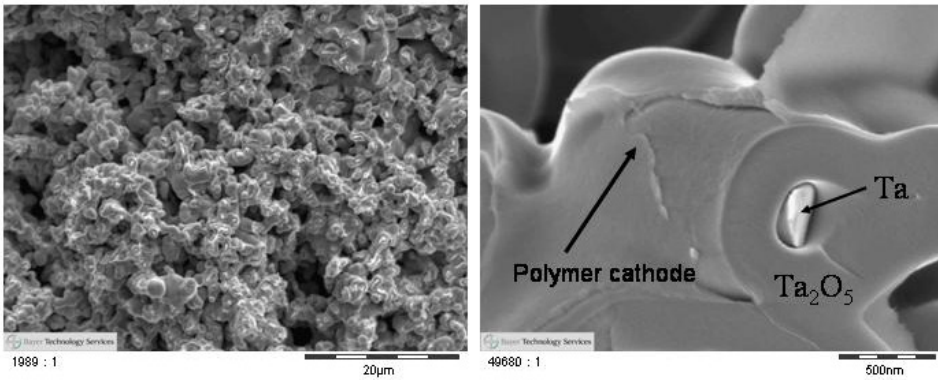


Fig.2: SEM pictures of the porous structure of a tantalum anode coated with a cathode film made from a conducting polymer dispersion

	conducting polymer dispersion	in-situ polymerization without reformation	in-situ polymerization with 50V reformation	in-situ polymerization with 75V reformation
capacitance [μ F]	15	15	15	14
ESR [$m\Omega$]	39	38	32	500
break-down voltage [V]	96	0	62	89

Table 1: Electrical properties of capacitors made by a polymer dispersion and by in-situ polymerizations (details see text)

High Voltage Applications

Initially our new dispersion of nano-scale conducting polymers was developed for low-capacitance tantalum powders. Typically these powders are used for high voltage applications. The average pore sizes of the low-capacitance powders are large compared to the size of the conducting particles so that impregnation is facilitated. We have found

remarkable properties of our dispersions for high voltage applications: high voltage polymer capacitors, i.e. capacitors with rated voltages higher than 20V, can be manufactured by the application of our polymer dispersions easily. With in-situ polymerization this is hardly possible since the polymerization degrades the quality of the dielectric oxide layer. Reformation processes for the dielectric oxide layer that are applied for low-voltage anodes fail at higher voltages.

In table 1 experimental results are shown for anodes made of a 30 000 $\mu\text{C/g}$ tantalum powder. The dielectric oxide layer was formed by anodization of the tantalum anodes at 100V. Capacitors made with our conducting polymer dispersion showed a low ESR and high break-down voltage. Capacitors whose cathode layer was formed by in-situ polymerization were short circuited. A reformation process during manufacturing increased the break-down voltage of the capacitors made by in-situ polymerization. The higher the reformation voltage was, the more the break-down voltage could be increased. But at high reformation voltages ESR performance is destroyed completely.

We developed a simple model to explain these experimental results (see figure 3): Cracks or pinholes are generated in the dielectric oxide layer during anodization of the tantalum anode. When in-situ polymerization is applied to form a cathode layer on top of the dielectric oxide layer the monomeric precursors of the conducting polymer can enter these cracks or pinholes and form a conducting path within the dielectric. So the break-down voltage of the dielectric is reduced.

The quality of the oxide can be recovered when a reformation voltage is applied over the dielectric: the resulting electrical current destroys the conducting polymer within the crack or pinhole. For very thick oxide layers, i.e. for high voltage applications, the cracks or pinholes get big. Now the current through the crack or pinholes has to be so high that the conductivity of the polymer cathode layer suffers significantly and ESR increases.

So the particle property of our new polymer dispersions and its high electrical conductivity do not only simplify the manufacturing process for polymer electrolyte capacitors but open up the field of high voltage applications. We demonstrated that tantalum polymer capacitors with 25 V and 35 V rated voltage, low ESR and DC leakage can be manufactured easily (see table 2).

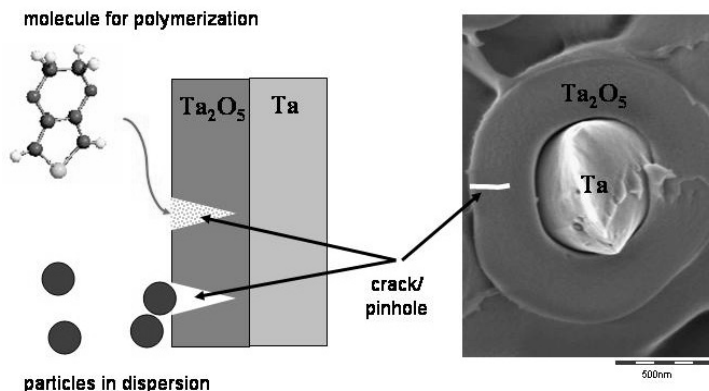


Fig. 3: Model for degradation of high-voltage dielectric oxide layer (details see text)

22μF/25V capacitor	15μF/35V capacitor
40 000 μ C/g powder 75 V anodization	30 000 μ C/g powder 100 V anodization
CAP: 25 μ F D.F.: 3.5 % ESR: 38 m Ω DCL: 0.4 μ A	CAP: 17 μ F D.F.: 3.0 % ESR: 44 m Ω DCL: 0.5 μ A

Table 2: High-voltage polymer electrolyte capacitors made by polymer dispersions (V case size)

High-Capacitance Tantalum Powders

Due to the ongoing trend to miniaturization in electronics the surface area of tantalum powders has been increased significantly over last decade [2]. Tantalum powders with a specific capacitance of up to 150 000 μ C/g have been introduced to the market successfully. The average pore size of the anodes decreases with increasing surface area: While a high-voltage powder anode with a specific charge of 30 000 μ C/g has an average pore size of about 1 μ m, the pore size of a 50 000 μ C/g and a 100 000 μ C/g anode is only about 0.6 μ m and 0.3 μ m respectively. We have developed conducting polymer dispersions as well as specific deposition processes that allow for the impregnation of such high-surface tantalum anodes.

For 50 000 μ C/g powder anodes we are able to achieve similar or better results as with in-situ chemical polymerization (see table 3). For 100 000 μ C/g powder anode capacitance recovery is still slightly lower and ESR higher with polymer dispersion than for in-situ chemical polymerization. Most recent data will be presented at the conference.

	capacitance [μ F]	ESR [m Ω]
in-situ polymerization	86	18
polymer dispersion	92	18

Table 3: Comparison of electrical performance of in-situ polymerization and polymer dispersion process for 50 000 μ C/g tantalum anodes (V case size)

	capacitance [μF]	ESR [m Ω]
in-situ polymerization	25	78
polymer dispersion	21	85

Table 4: Comparison of electrical performance of in-situ polymerization and polymer dispersion process for 100 000 $\mu\text{C/g}$ tantalum anodes (A case size)

Conclusions

The manufacturing process of conducting polymer electrolyte capacitors can be greatly simplified by conducting polymer dispersions. We have successfully developed conducting polymer dispersions that can impregnate even highly porous tantalum powder anodes and form polymer cathode layer with low ESR. Furthermore with our dispersions high-voltage polymer capacitors are feasible for the first time.

References

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