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Microstructure of PE-separators

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Abstract

The structure of polyvinylchloride (PVC) and polyethylene (PE)-separators was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). PE-separators are built up of a nanometer structured network of PE and silica. Carbon black is distributed equally with in the structure. After oxidation cracks appear which decrease the mechanical strength of PE-separator.

Keywords: PVC-separator; PE-separator; TEM structure; SEM-structure; Oxidation; Carbon distribution; Elemental maps

1. Introduction

Polyvinylchloride (PVC) and polyethylene (PE)-separators have been the most commonly used separators in automotive batteries for the last 20 years. Both separators are membranes with a narrow range pore size distribution. PVC-separators are produced by a sintering process of fine PVC-powders–PE-separators are produced by an extrusion process.

Figs. 1 and 2 show the typical structure of a sintered PVC-separator. The PVC-separator is built up by sintering PVC-powder of a particle size ranging between 10 and 20 μm. The decrease of particle size in the sintered product is negligible compared to the particle size of the raw materials. The pores are dispersed homogeneously with a medium size ranging between 10 and 20 μm (10,000–20,000 nm). Since a PVC-separator exclusively consists of PVC, it exhibits advantageously good chemical resistance against acid and alkaline solutions.

PE-battery separators are basically produced on the basis of the following raw materials: silica SiO_2, ultra high molecular weight (UHMW)-PE, mineral oil, carbon black. The raw materials are carefully mixed with a surplus of mineral oil and then extruded. Excess oil is removed by a solvent and, after drying, a separator of the following composition is formed:

- SiO_2 62–68%;
- UHMW-PE 20–25%;
- mineral oil 12–20%;
- carbon black 0.2–0.6%.

Raw material powders for production of PE-separators have a medium grain size of:

- SiO_2 10–30 μm (10,000–30,000 nm);
- PE ∼150 μm (150,000 nm);
- carbon black 0.01–0.09 μm (10–90 nm).

The PE-separator is a porous membrane with a medium pore size of approximately 0.1 μm (=100 nm) and a specific surface area of approximately 75 m^2/g. The goal of the investigation is to look into the structure of a finished PE-separator and determine the distribution of the different elements.

Fig. 3 shows the sponge-structure of a PE-separator with pores of around 0.1 μm diameter. PE melts in the course of processing. The inorganic fillers, SiO_2 and carbon, are distributed in a PE matrix. Transmission electron microscopy (TEM) pictures are used to evaluate the micro/nano system. The thickness of the different samples is approximately 100 nm. The samples are embedded in epoxy resin and sections are prepared with an ultra microton. Fig. 4 shows a TEM picture of a PE-separator. The homogeneous distribution of silica particles is evident, the pores appear light.

In Fig. 5 a TEM picture of a PE-separator with a lower mechanical strength is shown. The comparison between the structures of a PE-separator with good mechanical strength (high tensile strength, high elongation—Fig. 4) and a separator with lower mechanical strength—Fig. 5 demonstrates that both the amount and the size of pores, as well as the structure of the network, affect the mechanical strength. Tensile strength and elongation decrease as macropores are present, and homogeneity is lower.

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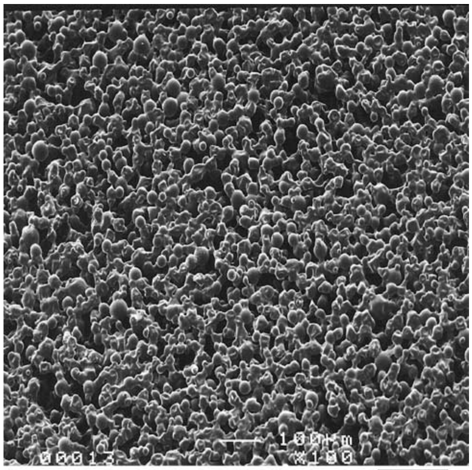

Fig. 1. PVC-separator 100 µm.

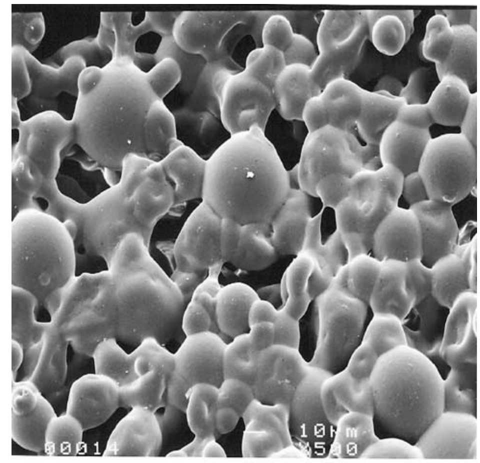

Fig. 2. PVC-separator 10 µm.

If we look at the distribution of silica and carbon in the 100 nm range (Fig. 6; silica–yellow, carbon–blue) we find a nano-disperse distribution of silica and carbon.

In production, the raw material silica powder initially consists of 10–15 µm particles and is then dispersed down to nm range. In all element-specific TEM pictures, no coarse particles of carbon black could be detected at any time. Carbon and silica are both distributed to nano-structured particles.

In Fig. 7, a PE-separator material in the 50 nm (0.05 µm) range is shown. In the TEM pictures—left side: the pores appear light with electron filtering transmission electron microscopy technique (EFTEM); right side: the pores appear black. We can still see silica particles in the nanometer range.

A PE-separator can be tested for oxidation stability by means of different procedures using strong oxidants like H_2O_2 or $K_2Cr_2O_7$. The grey colour of the PE-separator

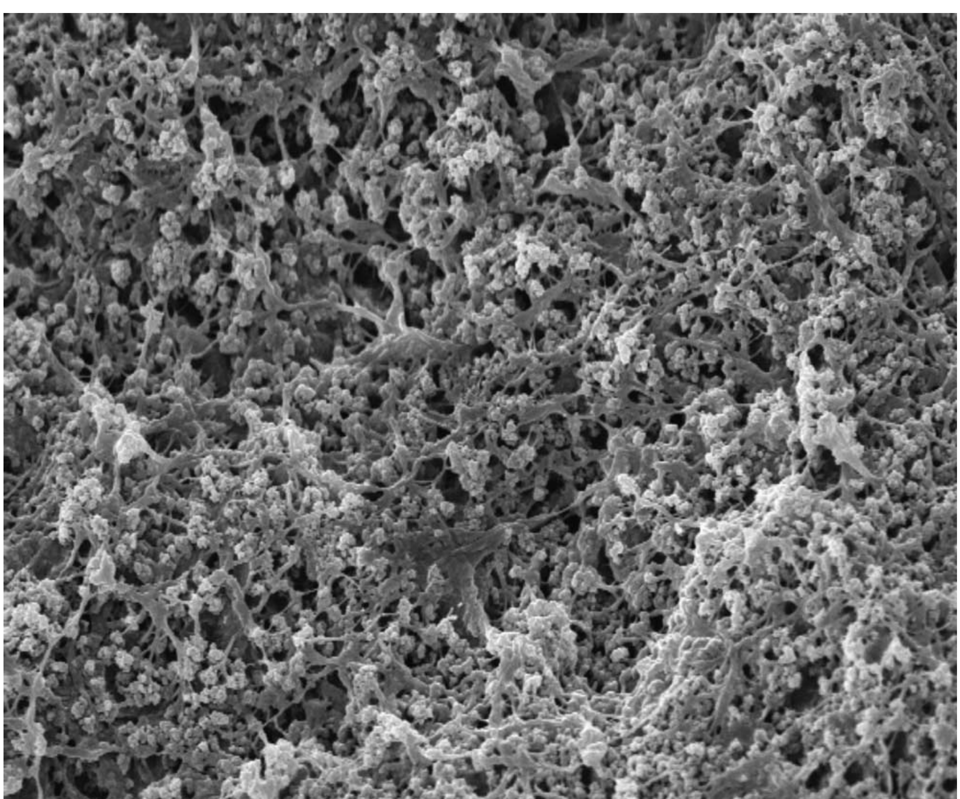

Fig. 3. PE-separator 2 µm.

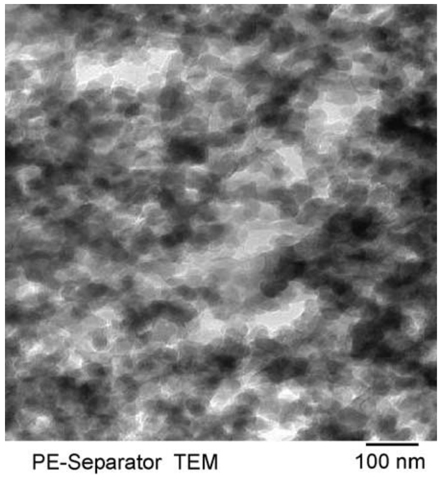

Fig. 4. PE-separator TEM 100 nm.

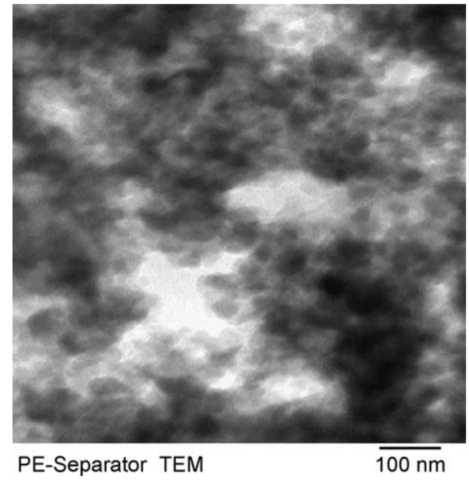

Fig. 5. PE-separator TEM 100 nm.

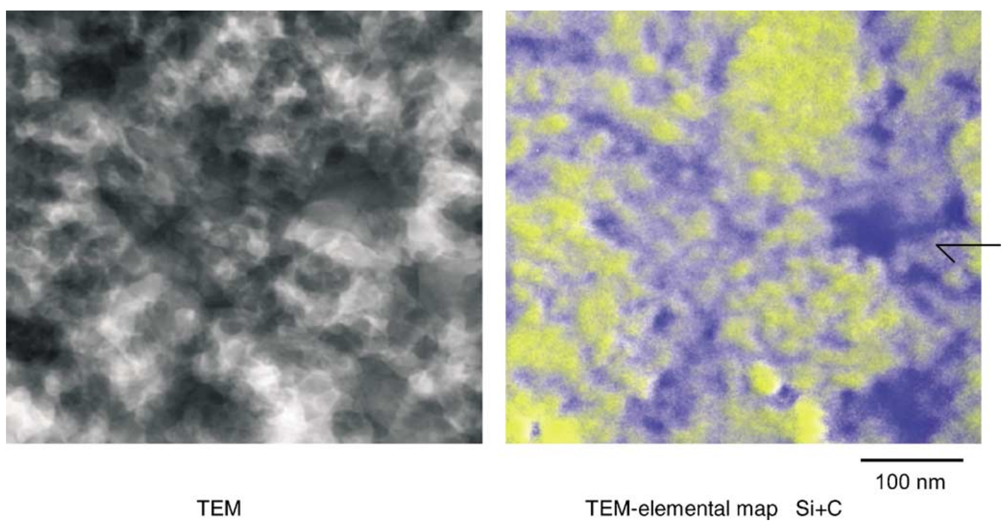

Fig. 6. TEM-elemental map Si + C 100 nm.

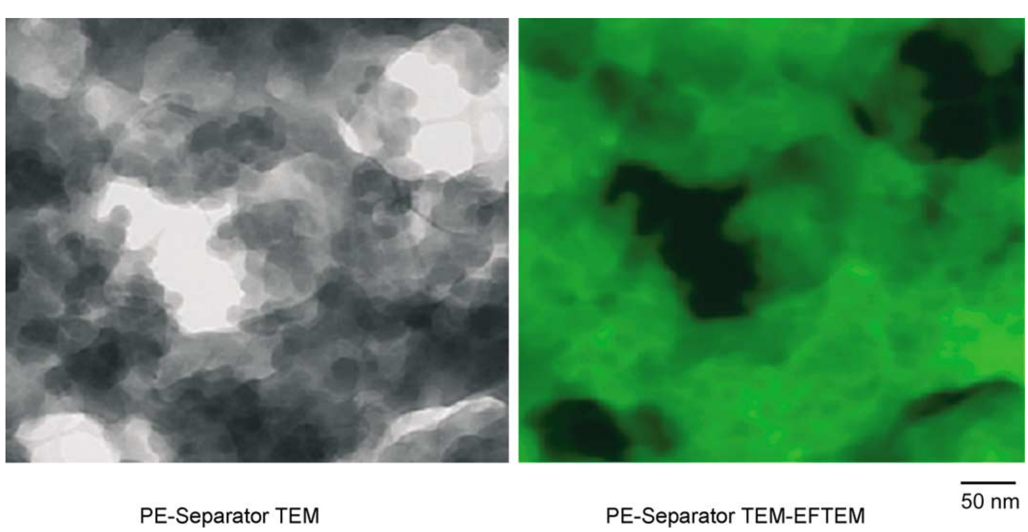

Fig. 7. PE-separator TEM, PE-separator TEM–EFTEM 50 nm.

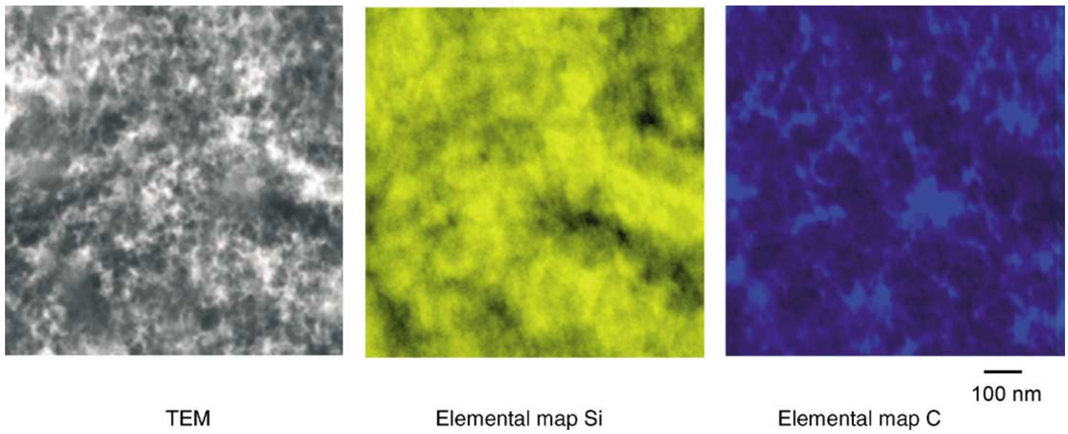

Fig. 8. TEM elemental map Si; elemental map C 100 nm.

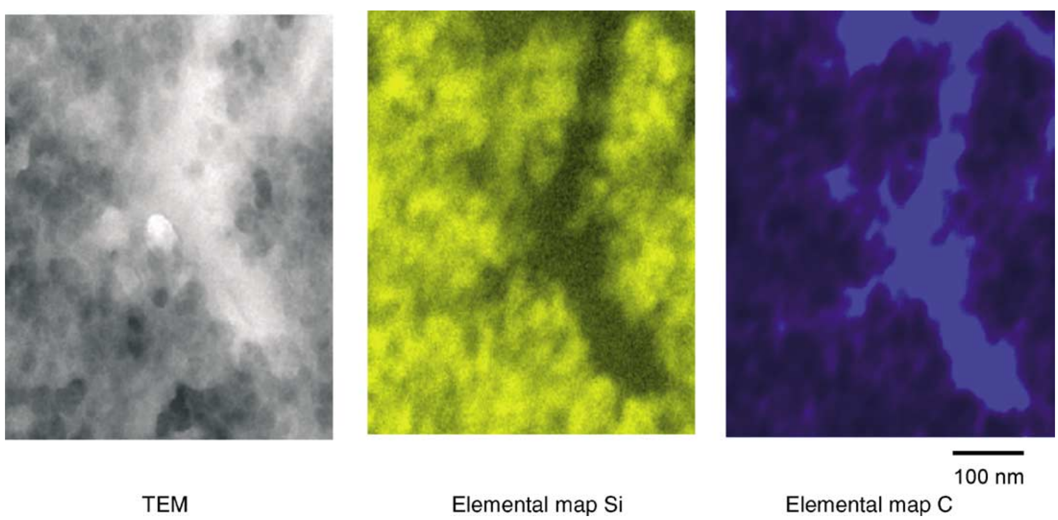

Fig. 9. TEM elemental map Si, elemental map C 100 nm.

caused by black carbon fades away during this procedure. During oxidation of a PE-separator, the homogeneous spongy structure of the separator is cracked.

Fig. 8 shows an unoxidised PE-separator. Fig. 9 shows an elemental map of a PE-separator after 24 h heavy oxidation. In Fig. 9, the cracks in the C-map appear blue as a result of the embedding of epoxy resin used in sample preparation. In an extended number of different exposures of separators after oxidation some aggregation of silica particles has been observed.

2. Conclusions

Based on TEM imaging of PE-separators, the following can be concluded:

1. The structure of silica, carbon and PE is in the nm range.
2. Carbon and silica are randomly distributed in a PE-filament matrix in a nanometer particle range.
3. No particles of carbon black can be observed, carbon black is also distributed in nm range in the PE-network.
4. During oxidation, the PE-network matrix is attacked, which leads to the formation of pores and cracks.
5. PE matrix and carbon-black are oxidised at the same time—no particles are left.
6. During oxidation, silica aggregates occur.
7. Mechanical strength decreases during oxidation due to the formation of macropores and cracks.