

Development of an alternative binder for lithium ion batteries based on epoxy resin

F. Bunzel*, M. Wagner*, E. Stammen* and K. Dilger*

*Technische Universität Braunschweig, Institute of Joining and Welding,
Braunschweig, Germany, f.bunzel@tu-braunschweig.de

ABSTRACT

The development of batteries for the e-mobility continuously creates new challenges for the researchers. To improve the performance of lithium ion batteries, different approaches might be considered. Therefore the Institute of Joining and Welding (ifs) focuses its research on the development of alternative binders for active materials.

Hence, different reactive adhesive systems were characterized on the basis of acrylates, epoxy resins and silicones with different curing mechanisms and were examined for the use as a binder. However, epoxy resins in particular showed a good performance. On account of the possibility of being able to adjust the properties of epoxy resins to a certain extent, this system was investigated in more detail. The results of the present study indicated that the use of epoxy resins is beneficial in terms of their properties and the simplified process technology via using PVdF. It is possible to adjust the properties of the epoxy resin to use it as a binder in lithium ion batteries.

Keywords: lithium ion battery, binder, adhesive, epoxy resin

1 INTRODUCTION

The development of batteries for the e-mobility continuously creates new challenges for the researchers. To improve the performance of lithium ion batteries, such as higher energy/power density and longer shelf/cycle life, intense research has been focused on the development of different cell materials, such as positive and negative electrode active material, separators and electrolytes. So far, much less attention has been given to the binders, the electrochemically inactive material. The function of the binder is to bond the electrode particles, second to bond the active material to its substrate. Furthermore, the binder is responsible for the life cycle. The life cycle of a lithium ion battery is determined by different degradation mechanisms in the cell. The electrochemical properties of the cell, as for example the available capacity, energy and power or the mechanical integrity of the cell deteriorate due to these degradation reactions. The causes of ageing of the cell are the dynamic stresses with charge and discharge and the structural changes caused thereby. Furthermore, the interaction between electrode and electrolyte and the chemical decomposition reactions originating from it and the modification of surface films contributes to the ageing. For example, the intercalation of lithium ions results in

volume expansion of the electrode material from which macroscopic shear forces result by which the contact of the particle in the active material between them, the contact between active material and binder and further the contact of the binder with the substrate deteriorates and thus the electron conductivity strongly decreases [1-2].

To raise the life cycle of a lithium ion battery, the degradation mechanisms described above must be prevented. One way of doing this is to substitute the generally used binder. However, this binder must show several requirements. On the one hand the binder in a lithium ion battery must provide the mechanical stability of the electrode, on the other hand it must guarantee the bonding of the particles of electrochemically active components to each other as well as to the current collector. Generally used binders are based on fluorinated polymers and copolymers, above all polyvinylidene fluorid (PVdF) and polyvinylidene fluorid-hexafluoropropylene (PVdF-HFP) [3-5]. From an ecological and economic point of view the application of the so-called fluorinated polymers is questionable, because their processing requires the use of organic solvents like N-methylpyrrolidone-2-on (NMP). NMP is identified as a substance of very high concern. Hence, there are numerous efforts to use healthwise safe binder systems and thus to improve the aspect of the environmental compatibility. In the literature numerous alternative binder systems are described for the anode as well for the cathode.

On the one hand different water-soluble binder systems were examined, mostly based on renewable raw materials. These include, for example, sodium carboxymethyl cellulose (Na-CMC) [4], [6-13]. To improve the mechanical stability a styrene butadiene rubber (SBR) is added. In the anode as well as in the cathode, the Na-CMC shows an adhesive strength similar to that of the PVdF, however, the interaction to the active material is much stronger due to the high number of hydroxyl groups, and moreover the ion conductivity is higher than with the PVdF. In addition Na-CMC is significantly more elastic than PVdF, so that a higher stability and a longer life cycle are achieved. Another advantage of the Na-CMC is the discontinuation of calendaring which otherwise would be necessary, due to the drying shrinkage of the binder. Other water-soluble binders based on renewable raw materials are alginate [14], chitosan [15], catechol [16] which show similar properties to an Na-CMC. Besides the water-soluble binders, only a few alternative polymers soluble in other solvents were used as binders in lithium ion batteries. A usable binder is a polyvinyl carbonate [17]. It was used as a binder in the

graphite anode and led to a higher capacity as well as a much better performance at low temperatures in comparison to PVdF. Polysiloxane cross-linked with epoxide could be successfully used as a binder [18]. Toluene was used as solvent. It shows that, due to the flexibility of polysiloxane and due to the good chemical resistance of both components, a binder system with very good adhesion properties can be developed.

As regards operating completely without solvent, this work represents a very new approach. Reactive adhesive systems were investigated due to their low viscosity, high adhesion strength to aluminum and copper, high mechanical strength and chemical resistance. Furthermore, it is possible to modify the reactive adhesive systems very easily in view of curing time, elasticity and porosity. Different reactive adhesives are available, such as silicone, acrylate, PU and epoxide. In this work an epoxy resin was investigated in more detail.

2 EXPERIMENTAL

Active anode material – SMG (graphite powder) - was purchased from Hitachi Chemical Co. The active cathode material – LMO - was purchased from Toda Kogyo Corp. PVDF binder was supplied by Arkema, two-component epoxy resin, flexibilizer and foamer were purchased from R&G. Isopropyl alcohol was supplied by Merck.

For swelling experiments small plates of cured adhesives were stored in dimethylcarbonate (DMC) for 72 h. DMC was acquired from Merck. The thickness of the small plates was measured before and after swelling, and ATR spectra (Bruker Tensor 27) were also recorded.

Uniform slurries with different LMO/epoxy resin or graphite/epoxy resin ratios were made by adding dried LMO or graphite powder into the epoxy resin and then mixing them with a Speedmixer for 3 min. The slurries were then cast onto aluminum or copper foil using the doctor-blade method with a thickness of 200 μm . The adhesive was cured at 65°C in an oven for 12 h. The porosity was determined by a Laser Scanning Microscop (Keyence VK/9710).

For T-peel tests the slurries were cast between two foils with a thickness of 200 μm . The adhesion strength was determined using an Instron 5567.

For Dynamic Mechanical Analysis (DMA) measurements circular samples with a thickness of 2 mm were prepared. DMA measurements were carried out in shear mode with a fixed frequency of 1 Hz and a heating rate of 2 K/min.

3 RESULTS AND DISCUSSION

Various adhesives were investigated as regards the use of a binder in lithium-ion batteries, e.g. silicone, acrylates and epoxides. First of all the chemical resistance of the adhesives was validated. Swelling experiments shows that acrylates are not stable in the electrolyte. The ATR

spectrum (Figure 1) shows degradation of the acrylate chain. The acrylate sample decomposed completely in the electrolyte. In contrast, an epoxide adhesive is stable in the electrolyte. The ATR spectrum shows no differences before and after the swelling test (Figure 2). Hence, only the epoxide adhesive is applicable as a binder in lithium-ion batteries.

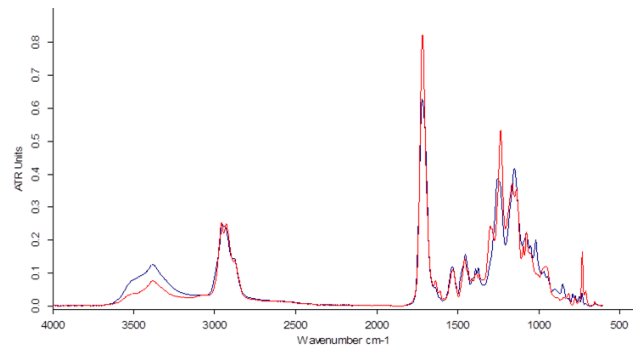


Figure 1: ATR spectrum of an acrylate adhesive; blue line before swelling, red line after 72 h swelling.

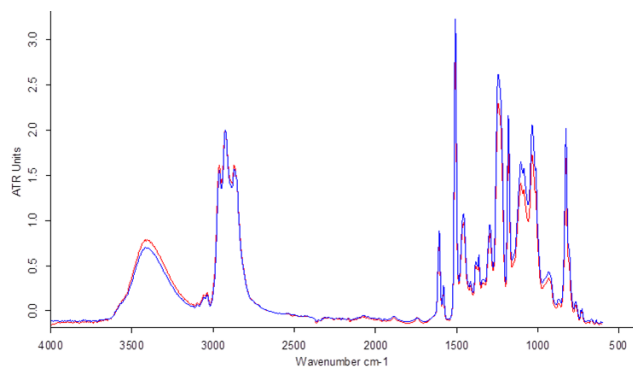


Figure 2: ATR spectrum of an epoxide adhesive; blue line before swelling, red line after 72 h swelling.

Mixtures with different contents of LMO and graphite were prepared. Up to 60 % graphite and 70 % LMO no solvent is necessary. For the preparation of a mixture with a content of 80 % graphite or LMO, isopropyl alcohol was used as a solvent. Homogeneous mixtures were obtained with suitable viscosity for casting onto aluminum or copper foil using the doctor-blade method.

The adhesion strength was measured with a T-peel test (Figure 3). The results show that the adhesion strength improved with the use of a reactive epoxy resin as a binder. The adhesion strength is higher to aluminum foil than to copper foil and with increasing the content of the active electrode material a decrease of the adhesion strength is obtained. Different surface pretreatments, such as flame treatment and plasma, improve the adhesion strength. The best results were obtained with flame treatment. Hence, a delamination could be reduced with the use of a reactive epoxy resin.

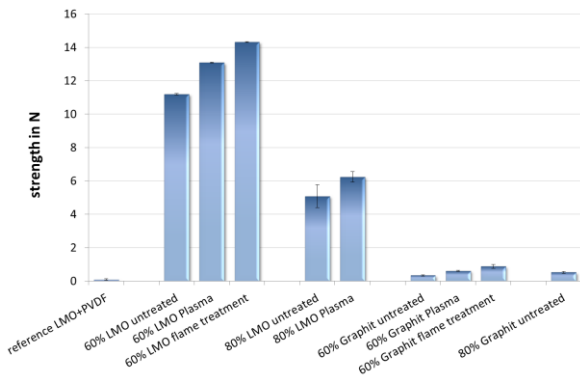


Figure 3: Adhesion strength determined by T-peel test

To get a sufficient porosity without a solvent, a foamer was used. The LSM images show that without a foamer low porosity of the coating can be seen (Figure 4b). By adding a foamer the porosity increased (Figure 4c) and is comparable to the reference (Figure 4a).

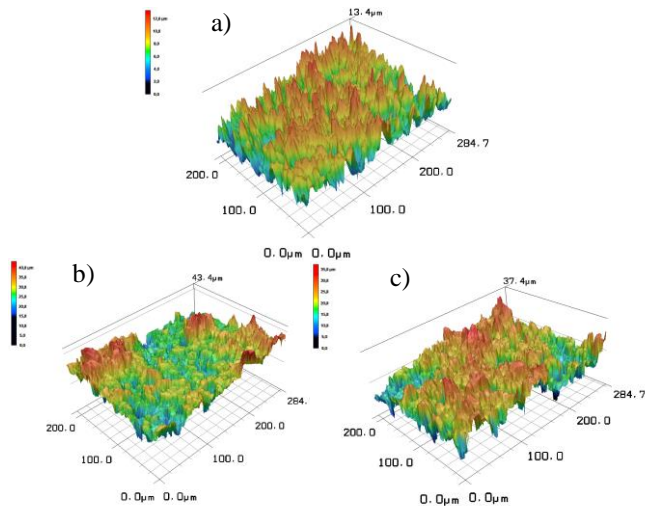


Figure 4: LSM images of a) PVdF graphite, b) epoxy graphite and c) epoxy graphite with foamer

An epoxy resin is normally very strong but brittle. To get a flexible binder in order to avoid crack formation by charging and discharging additives were used to modify the epoxy resin. By means of DMA measurements the elasticity and the T_g can be determined. Mixtures with LMO and graphite were investigated.

In Figure 5 the DMA curves of epoxy-LMO mixtures are shown. With increasing content of LMO the T_g decreases significantly, but the storage module E' increases. This indicates an interaction between LMO and epoxy resin. Hence, the chemical structure and thus the properties of the epoxy resin are influenced by the LMO. Due to a high content of LMO the mechanical strength of the cured epoxy resin deteriorates, because at 0 °C the storage module E' decreases significantly. With the addition of a flexibilizer the T_g decreases, too. But the change is not so

significant. Furthermore, the storage module increases by adding a flexibilizer.

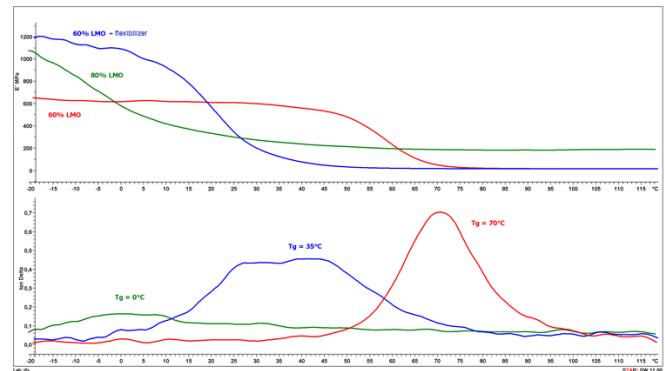


Figure 5: DMA curves of different epoxy-LMO mixtures, red: 60 % LMO, green: 80 % LMO and blue: 60 % LMO with flexibilizer

In Figure 6 the DMA curves of different epoxy-graphite mixtures are shown. In this case the T_g and the storage module show no shifting with increasing content of graphite. The chemical structure and thus the properties of the epoxy resin are not influenced by the graphite. By addition of a flexibilizer the T_g decreases and the storage module increases slightly.

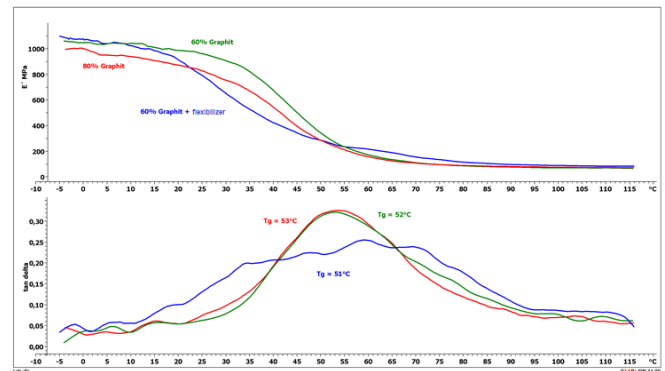


Figure 6: DMA curves of different epoxy-graphite mixtures, red: 60 % graphite, green: 80 % graphite and blue: 60 % graphite with flexibilizer

The DMA measurements show that it is possible to get a flexible binder by the addition of a flexibilizer in order to avoid crack formation.

4 CONCLUSIONS

Reactive adhesion systems such as epoxy resins are suitable for being used as a binder in lithium-ion batteries. Epoxy resins are chemically resistant and miscible with active electrode materials. They show a very high adhesive strength to aluminum and copper foil. The porosity of the coating can be adjusted by different foaming agents. The elasticity of the epoxy resin can be set by different

flexibilizers. Advantages of an epoxy resin as binder in lithium-ion batteries are the chemical resistance, high adhesion strength, elasticity and no solvent is necessary. Hence, the life cycle of a lithium-ion battery with an epoxy resin as binder should be improved.

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