Mechanical and Electrical Properties of Poly(vinylidene fluoride–tetrafluoroethylene–propylene)/Super-S Carbon Black Swelled in Liquid Solvent as an Electrode Binder for Lithium-Ion Batteries

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ABSTRACT: The mechanical and electrical properties of poly(vinylidene fluoride–tetrafluoroethylene–propylene) (PVDF–TFE–P) and carbon black–filled PVDF–TFE–P composites were investigated. The carbon black was used for its electrolyte absorption properties in addition to boosting the conductivity. This elastomeric binder system may have application to tin- or silicon-based electrode materials for Li-ion batteries, which undergo huge volumetric changes during charge/discharge cycling. The mechanical and electrical properties were measured while film samples were immersed in a liquid solvent (ethylene carbonate : diethyl carbonate 1 : 2) commonly used in the battery electrolyte. Uncrosslinked PVDF–TFE–P uptakes about 140% solvent by mass and swells significantly. The amount of solvent absorbed can be reduced and the mechanical properties improved by crosslinking the polymer. Two crosslinking recipes, based on bisphenol and triethylenetetramine (TETA), were investigated carefully. Compared to the bisphenol-based crosslinking recipe, the proposed TETA-based crosslinking recipe gave films with a higher degree of crosslinking and better mechanical properties. The TETA-crosslinked composites had very good mechanical and electrical reversibility even during cyclic deformation to 100% strain. The cycling results of amorphous $Si_{0.64}Sn_{0.36}$ electrodes show that the capacity retention of the electrodes can be significantly improved by using the proposed elastomeric binder. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2958–2965, 2004

Key words: poly(vinylidene fluoride–tetrafluoroethylene–propylene) (PVDF–TFE–P); bisphenol; crosslinking; swelling; composite electrode

INTRODUCTION

Carbon-filled polymer composites have attracted attention because of their excellent mechanical properties and electrical conductivity.[1–5] In lithium-ion batteries, carbon black–filled polymer composites are widely used as electrode binders.[6,7] Carbon black is normally used as a conductive filler to provide an electronic pathway between the active material particles and the current collector. In some electrodes, carbon black is also used to absorb large quantities of electrolyte. Elasticity of the binder is desired to maintain electrode integrity during charge/discharge cycles.

Recently, significant attention has been given to metallic alloy anode materials as possible replacements for graphite.[8–12] For instance, amorphous (a-) $Si_{0.67}Sn_{0.33}$ can deliver a capacity of about 2000 mA h g^{-1} [10,11] and shows good charge/discharge cycling as a thin sputtered film. However, it appears to us that ultimately, alloy materials must be incorporated as composite electrodes made from small ($\sim 1 \ \mu m$) particles to minimize solid-state diffusion lengths for lithium and ensure good rate capability for the resulting battery. Composite electrodes of $Si_{0.67}Sn_{0.33}$ using poly(vinylidene fluoride) (PVDF) binder show poor capacity retention with cycle number, which we believe is caused by the huge volumetric changes (>250%) of the electrode particles during charge/discharge cycles.[11] Even though the particles of this amorphous alloy do not fracture during expansion and contraction,[11] electrical contact to the particles is lost, we believe, because of the poor mechanical properties of the PVDF binder.[13,14]

Recently, we reported crosslinked poly(vinylidene fluoride–tetrafluoroethylene–propylene) (PVDF–TFE–P) as a promising binder for electrode materials that show large volumetric changes during charge/discharge cycling.[13,14] If the carbon black–filled PVDF–TFE–P composite is properly crosslinked, composite films can be

stretched to 160% strain before breaking. By contrast, the commonly used PVDF, with or without added carbon black, breaks at about 5% strain. As a component of battery electrodes, the carbon-filled PVDF–TFE–P composite will eventually be exposed to nonaqueous liquid solvents used as electrolytes in lithium-ion batteries. Thus, it is of great interest to study the mechanical and electrical properties of the carbon/polymer composites immersed in the liquid solvent.

The swelling of polymers in liquid solvents has been extensively reported in the literature.[15–19] When a polymer is exposed to a liquid solvent, the solvent is absorbed and interacts with the polymer chains. The properties of the polymer are usually significantly affected. The expansion of the polymer after swelling can be easily observed.[16,17] If the polymer is filled with a conductive component, such as carbon black, a dimensional expansion causes a decrease in the effective volume fraction of the conductive fillers. Hence, a decrease of electrical conductivity after swelling can be expected according to percolation theory. In addition, the interaction of solvent molecules and polymer chains weakens the interaction between the polymer chains, especially in uncrosslinked linear polymers. After swelling, some of the polymer chains can slide over each other and release physical entanglements. A decrease of the elastic modulus during solvent uptake is reasonably expected.[19]

The main aim of this work was to evaluate the mechanical and electrical properties of crosslinked PVDF–TFE–P and carbon black–filled PVDF–TFE–P composites in a "real" environment, the liquid solvent for lithium-ion batteries. In addition, efforts were also made to establish criteria to optimize polymeric binders for amorphous alloy anode materials.

EXPERIMENTAL

A PVDF–TFE–P polymer (BRE-7131X, 60% fluorine; Dyneon Co., Oakdale, MN) was used in this study. The details of the polymer (relative monomer content, molecular weight) were not made available to us. Two crosslinking recipes based on bisphenol and triethylenetetramine (TETA, Aldrich, Milwaukee, WI) were adopted in this work. The bisphenol-based recipe was recommended by the manufacturer and the TETA-based recipe was proposed to increase the degree of crosslinking.

Preparation of TETA-crosslinked BRE-7131X and BRE-7131X/carbon black films

A BRE-7131X slab obtained from the manufacturer was cut into small pieces and dissolved in methyl ethyl ketone (MEK; Aldrich Chemical, Milwaukee, WI) to make a solution containing 20% BRE-7131X by weight. Then 3 pph (parts per hundred mass of BRE-

7131X) 1,4-diazabicyclo[2.2.2]octane (DABCO; Aldrich), 4 pph CaO (Fisher Scientific, Pittsburgh, PA), a determined amount of TETA, and 25 pph Super-S carbon black (SS; MMM Carbon, Brussels, Belgium), if desired, were added to the BRE-7131X solution and mixed for 1 h. The final mixture was then cast onto a piece of Teflon release film (3M Co., St. Paul, MN) using a spreader bar with a gap of 0.016 in., and dried in air overnight.

Preparation of bisphenol-crosslinked BRE-7131X and BRE-7131X/SS films

A BRE-7131X slab obtained from the manufacturer was cut into small pieces and dissolved in MEK to make a solution containing 20% BRE-7131X by weight. Then 6 pph MgO (Maglite Y; C. P. Hall Co., Bedford Park, IL), 2 pph CaO (Fisher Scientific), and 25 pph SS, if desired, were added to the BRE-7131X solution and mixed. Films were cast as above and dried in air, and then heated under a flow of argon in a tube furnace at 110°C.

Preparation of conventional a-$Si_{0.64}Sn_{0.36}$ electrodes incorporating PVDF binder

PVDF powder (Solef 1008/1001; Solvay Solexis Co., Brussels, Belgium) was dissolved in N-methyl pyrrollidinone (NMP; Aldrich) to form a solution containing 10% PVDF by weight. a-$Si_{0.64}Sn_{0.36}$ (0.3 g) was mixed with 0.3 g PVDF solution, 0.060 g SS, and 0.75 g NMP. After shaking for 15 min, the final mixture was then cast onto a piece of copper foil using a notch bar spreader with a gap of 0.4 mm. After that, the film was dried in an oven at 90°C overnight before use. The mass of a-$Si_{0.64}Sn_{0.36}$ per unit area of the electrode was 5.67 mg/cm^2.

Preparation of a-$Si_{0.64}Sn_{0.36}$ electrodes incorporating the TETA-crosslinked elastomeric binder

PVDF–TFE–P (1.0 g) was dissolved in 9.0 g MEK. Then, 0.04 g CaO and 0.03 g DABCO were added to the solution as crosslinking additives. a-$Si_{0.64}Sn_{0.36}$ (0.3 g; 3M Co.) was mixed with 0.3 g 10% PVDF–TFE–P solution, 0.06 g SS, 0.014 g 3-aminopropyltriethoxysilane (Aldrich), and 0.75 g MEK. 3-Aminopropyltriethoxysilane was used as an adhesion promoter to help binder the polymer to the surfaces of a-$Si_{0.64}Sn_{0.36}$ and SS. After shaking for 15 min, the final mixture was then cast onto a piece of copper foil using a notch bar spreader with a gap of 0.4 mm. The electrode was dried in air overnight and then heated at 110°C in Ar flow for 24 h before use. The mass of a-$Si_{0.64}Sn_{0.36}$ per unit area of the electrode was 5.55 mg/cm^2.
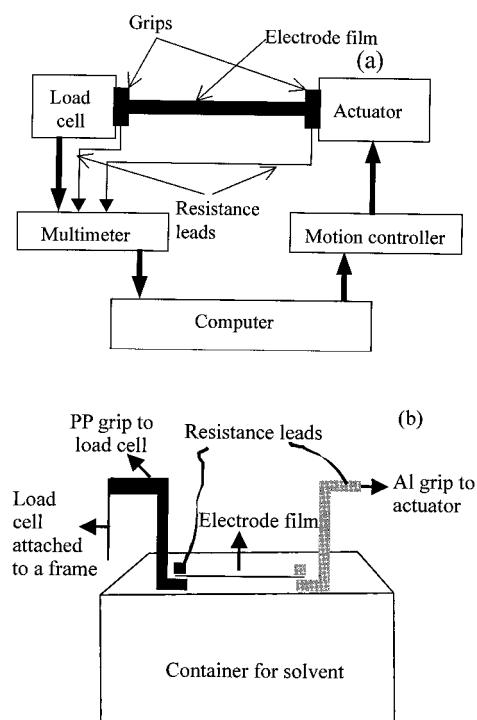
Figure 1 (a) Schematic of the stress–strain and resistivity tester. (b) The specially designed grips to study the mechanical and electrical properties of polymer films immersed in the liquid solvent.

Preparation of electrochemical test cells

Coin-type test cells were constructed using the electrodes in 2325 coin cell hardware. The cells used a polypropylene microporous separator, an electrolyte [$1M$ LiPF$_6$ dissolved in a 1 : 2 (v/v) mixture of ethylene carbonate and diethyl carbonate; Mitsubishi Chemical Co., Tokyo, Japan], and a lithium counterelectrode. The cells were assembled and crimped closed in an Ar-filled glove box.

Mechanical characterization

A homemade stress–strain and resistivity tester, as described in previous work,[14] was used to measure the mechanical and electrical properties of the binder films. Figure 1(a) shows a schematic diagram of the apparatus. The strain rate was set to ±0.05 min^{-1} to decrease the effect of solvent (i.e., DEC) evaporation. A good reference to the general features of the mechanical properties of polymers is the book by Ward and Hadley.[20]

Special modification was made to the sample grips, as schematically shown in Figure 1(b), to study the properties of the binder films swelled in liquid solvent. The solvent used was a mixture of ethylene carbonate (EC; Aldrich) and diethyl carbonate (DEC; Aldrich) with a ratio of 1 : 2 by volume. After the

sample was successfully mounted in the grips, the container with the liquid solvent was lifted and the sample film was immersed in the solvent for 5 min before the measurement started. During the experiment, some electrochemical reactions, such as the decomposition of the solvent, could occur if the potential difference between the Al grips reached over 4 V. Hence, the current used for the resistance measurement was set to a small value of 0.5 μA. Therefore, it is not unusual to see some noise in the nominal resistivity versus strain results because small voltage measurements were usually recorded. The nominal resistivity ρ_n is defined to be

$$\rho_n = \frac{RA_0}{L_0} \tag{1}$$

where R is the resistance measured in the experiment, A_0 is the original cross-sectional area of the tested film, and L_0 is the original distance between two sample grips.

To evaluate the amount of swelling of the crosslinked polymer films, the films were immersed in the mixed solvent [EC/DEC (1 : 2 by volume)] for 24 h. Then the film was dried quickly with a paper towel (<1 min) to eliminate the solvent drops on the surface. The mass of the film before and after soaking was measured to determine the percentage weight uptake of the films, which is defined here to be the swelling ratio. The typical mass of samples used for the soaking test was about 0.2 g.

RESULTS AND DISCUSSION

Swelling of crosslinked PVDF–TFE–P and carbon-filled PVDF–TFE–P composites

The crosslinked polymer samples were immersed in the EC/DEC (1 : 2 by volume) mixed solvent for 24 h, and then the change of weight, which was caused by the uptake of the solvent, was recorded. Figure 2 shows the swelling ratios of the crosslinked PVDF–TFE–P films as a function of the amount of crosslinking. For both sets of polymers, the amount of solvent absorbed decreases with increased crosslinking. The uncrosslinked film absorbs 140% solvent by weight, whereas the film crosslinked with 5 pph TETA absorbs 47% solvent by weight. The equilibrium-swelling ratio of the polymer can be controlled by the amount of crosslinking.

As mentioned above, the polymer can uptake more than 40% liquid solvent and this causes the volumetric expansion of the polymer. When the polymer is loaded with conductive fillers, such as Super-S carbon black, the resistivity of composites will change during swelling and can be used as an indicator to study the kinetics of the swelling of the composites in the liquid
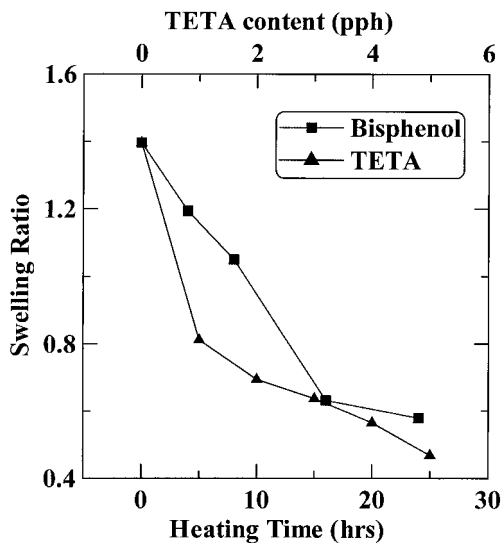
Figure 2 The swelling ratios of crosslinked PVDF–TFE–P in EC/DEC (1 : 2 by volume). (■) bisphenol crosslinking recipe; (▲) TETA crosslinking recipe. pph: parts per hundred mass of the polymer BRE-7131X.

Figure 3 Stress–strain curves of bisphenol-crosslinked PVDF–TFE–P heated at 110°C. The samples were immersed in EC/DEC (1 : 2 by volume) during the measurement.

solvent. Super-S carbon black (25 pph) was added to the samples crosslinked with bisphenol and TETA, respectively. For bisphenol-crosslinked PVDF–TFE–P/SS samples, the nominal resistivity increases rapidly and reaches its maximum in about 1 min. After that, the samples relax in the solvent and the nominal resistivity decreases slightly. However, it takes about 2 min for the TETA-crosslinked samples to reach their equilibrium-swelled states. All samples were believed to be completely swelled in the solvent within 5 min, and all the samples in the following sections were preswelled in EC/DEC (1 : 2 by volume) for 5 min before stress–strain and resistivity measurements.

Mechanical properties of bisphenol-crosslinked PVDF–TFE–P swelled in EC/DEC

Figure 3 shows the stress–strain curves of bisphenol-crosslinked PVDF–TFE–P films, which were swelled in EC/DEC (1 : 2 by volume) for 5 min before measurement. The stress–strain curves clearly indicate the dimensional change of the polymer films during swelling. Even though the films were mounted taut between the grips, upon immersion in the solvent the resulting expansion (about 20% in length) caused the films to go slack. This is why the stress in Figure 3 does not begin to increase until the strain (measured from the dry length) reaches about 20% when the new equilibrium length of the swelled film is reached. After that point, the stress increases almost linearly with the strain. When the polymer film was not heated, assuming that no or negligible crosslinking was introduced, the film swelled significantly (160%) in the solvent and the stress during stretching was small and
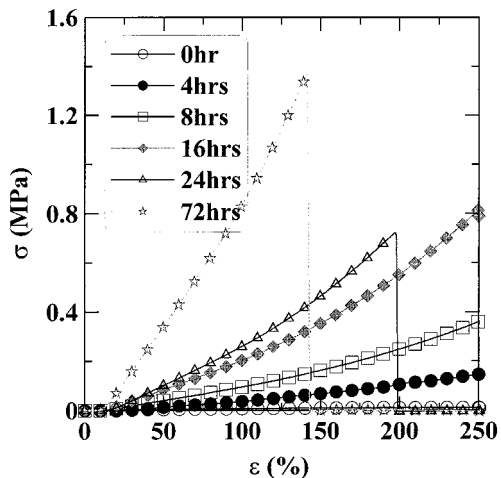
the film broke at a small strain. When the dry films, before measurement, were heated in argon at 110°C to introduce crosslinking, the elastic modulus (the slope of the curves in Fig. 3) increased with heating time. This is believed to be the effect of the crosslinking introduced. When the film was heated at 110°C for less than 16 h, the film could be stretched to 250% strain without breaking. However, if the film was heated longer to introduce more crosslinks, the film broke at a smaller strain. For example, a relatively high degree of crosslinking can be achieved by heating for 72 h, although the film breaks at about 140% strain.

Figure 4 shows the cyclic stress–strain curves of bisphenol-crosslinked PVDF–TFE–P in EC/DEC. Because a large breaking strain was desired for our ob-
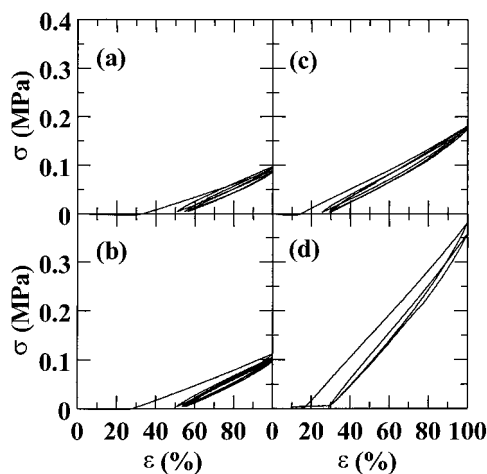

Figure 4 Cyclic stress–strain curves of bisphenol-crosslinked PVDF–TFE–P heated at 110°C for (a) 4 h, (b) 8 h, (c) 16 h, and (d) 24 h. The samples were immersed in EC/DEC (1 : 2 by volume) during the measurement.

jective, only the data for samples heated at 110°C for 4, 8, 16, 24 h [Fig. 5(a), (b), (c), and (d), respectively] are shown in Figure 4. All four samples studied could be cyclically deformed to 100% strain without breaking. The samples have almost the same reversibility during cyclic deformation, and may be acceptable for our application.

Mechanical properties of TETA-crosslinked PVDF–TFE–P swelled in EC/DEC

Figure 5 shows the stress–strain curves of TETA-crosslinked PVDF–TFE–P films swelled in EC/DEC. The elastic modulus of the films increases with the TETA content. When the content of TETA is less than 3 pph, the film can be stretched to 250% strain without breaking. When 4 or 5 pph TETA was added, the film broke at about 120% strain. Comparing the sample without TETA (TETA-crosslinking recipe in Fig. 5) to the sample without heating (bisphenol-crosslinking recipe in Fig. 3), one can see that the sample without TETA (Fig. 5) has a visible elastic modulus and a larger breaking strain (>250%). This suggests that a small amount of crosslinking was introduced even when no TETA was added under the preparation conditions. A possible explanation is that the highly basic conditions of the TETA-crosslinking recipe assists bisphenol, which was already incorporated in the polymer by the manufacturer, to introduce a small number of crosslinks at room temperature, even though a higher temperature is suggested with the recommended recipe.

Figure 6 shows the cyclic stress–strain curves of TETA-crosslinked PVDF–TFE–P in EC/DEC with the TETA content ranging from 0 to 4 pph. Because the breaking strain of the sample crosslinked with 5 pph
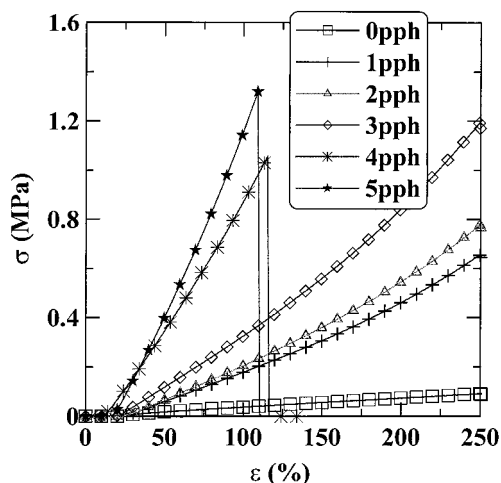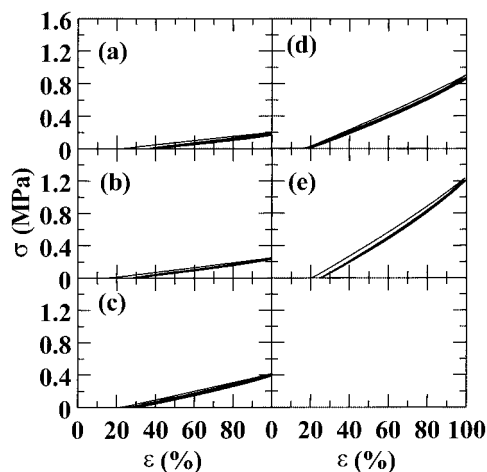

Figure 6 Cyclic stress–strain curves of TETA-crosslinked PVDF–TFE–P with (a) 0 pph, (b) 1 pph, (c) 2 pph, (d) 3 pph, and (e) 4 pph TETA. The samples were immersed in EC/DEC (1 : 2 by volume) during the measurement.

TETA was slightly larger than 100%, it could be stretched to 100% strain but broke during the second cycle. Hence, Figure 6 does not include the data for the sample with 5 pph TETA. Compared to samples crosslinked with bisphenol (Fig. 4), the TETA-crosslinked samples show almost no hysteresis during expansion and contraction. The films established their new equilibrium length at about 20% strain regardless of the amount of TETA added. After that, the stress increased linearly with the strain up to 100%. The most interesting point is that the stress–strain curve completely overlapped after the first stretching, and almost no hysteresis was observed.

Mechanical and electrical properties of bisphenol-crosslinked PVDF–TFE–P/SS swelled in EC/DEC

In a practical electrode for lithium-ion batteries, Super-S carbon black can be used as the conductive filler. It is important to study the mechanical and electrical properties of carbon-filled composites after swelling in EC/DEC.

Figure 7(a) shows the stress–strain curves of bisphenol-crosslinked PVDF–TFE–P filled with 25 pph Super-S carbon black. After swelling in EC/DEC, the films expanded by about 10% in the stretching direction. When the film is taut, the stress increases linearly with the strain. The elastic modulus, or the slope of the stress–strain curve, increases with the heating time for crosslinking. Even when the sample was heated for 24 h, the film broke at about 50% strain. Figure 7(b) shows the nominal resistivity of the composites after swelling and during strain. The nominal resistivity ranges from 6 to about 12 Ω cm during stretching. Because no sample can be stretched up to 100% strain,

Figure 5 Stress–strain curves of TETA-crosslinked PVDF–TFE–P. The samples were immersed in EC/DEC (1 : 2 by volume) during the measurement.
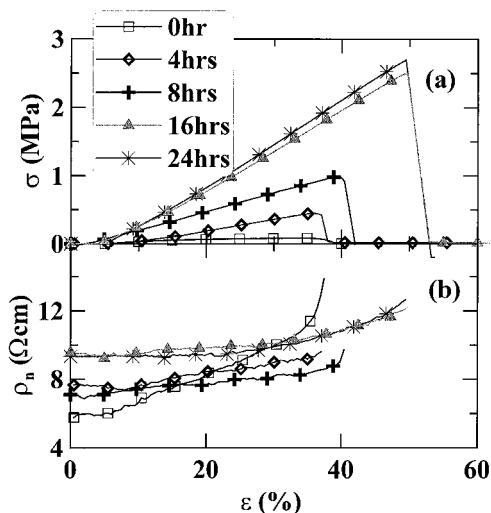
Figure 7 (a) Stress–strain and (b) nominal resistivity–strain curves of bisphenol-crosslinked PVDF–TFE–P/SS immersed in EC/DEC (1 : 2 by volume). Samples with 25 pph Super-S carbon black were heated at 110°C in argon for the times indicated in the legend.

Figure 9 Stress versus strain and nominal resistivity versus strain during cyclic deformation of TETA-crosslinked PVDF–TFE–P/SS composites immersed in EC/DEC (1 : 2 by volume). The samples had (a) 3 pph, (b) 4 pph, and (c) 5 pph TETA added. Super-S carbon black (25 pph) was added to the samples.

no data will be presented for the cyclic deformation of the bisphenol-crosslinked composites.

Mechanical and electrical properties of TETA-crosslinked PVDF–TFE–P/SS swelled in EC/DEC

Figure 8(a) shows the stress–strain curves of TETA-crosslinked PVDF–TFE–P/SS composites after swelling in EC/DEC. When the TETA content was less than 4 pph, the breaking strain of the swelled composites
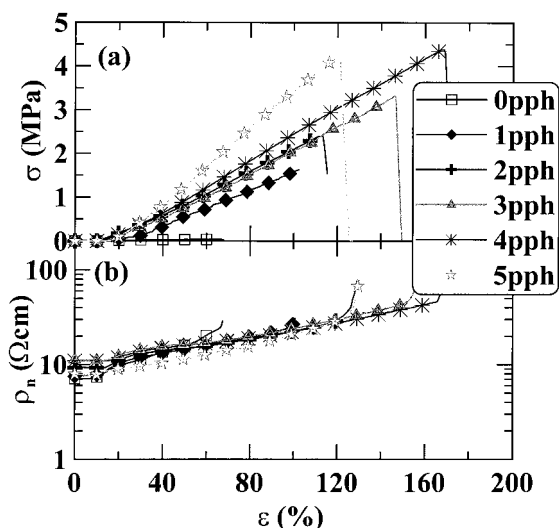

Figure 8 (a) Stress–strain and (b) nominal resistivity–strain curves of TETA-crosslinked PVDF–TFE–P/SS immersed in EC/DEC (1 : 2 by volume). Super-S carbon black (25 pph) was added to the samples. The amount of TETA added to each sample is indicated in the legend.
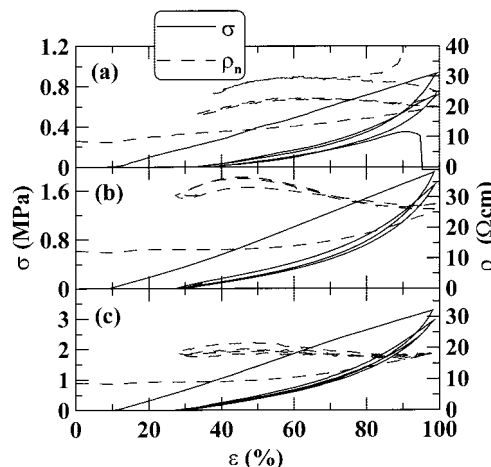
increased with the amount of TETA added. When 4 pph TETA was added, the composite film could be stretched to 170% strain before breaking. However, further addition of TETA to the composite decreased the breaking strain. When 5 pph TETA was added, the breaking strain decreased to about 125% strain. Figure 8(b) shows the nominal resistivity–strain curves of the swelled composites. All the curves approximately overlap each other. Apparently, the crosslinking introduced by TETA has little impact on the resistivity of the swelled composites.

Figure 9 shows the cyclic deformation of TETA-crosslinked PVDF–TFE–P/SS composites after swelling in EC/DEC. The samples with 3, 4, and 5 pph TETA have almost the same stress–strain profiles, except for the scales of the stress axes in Figure 9. The sample with 3 pph TETA could be cyclically deformed to 100% strain and broke during the third cycle. Samples with 4 and 5 pph TETA could be cyclically stretched to 100% strain and released without breaking. The nominal resistivity of TETA-crosslinked composites has very good reversibility after the first stretching and varies within the range of 20–30 Ω cm.

Electrochemical results for a-Si$_{0.64}$Sn$_{0.36}$ electrodes incorporating different binder systems

We believe that the TETA-crosslinked PVDF–TFE–P/SS composites have better mechanical properties than those crosslinked by bisphenol. Hence, only the TETA-crosslinked elastomeric binder was chosen to compare with the conventional binder PVDF.

Figure 10 shows the voltage versus specific capacity of a-Si$_{0.64}$Sn$_{0.36}$ electrodes using a Li counter and ref-

erence electrode. Both cells were first discharged to 0.22 V and then cycled between 0.2 and 1.0 V using a specific current of 60 mA/g. The a-$Si_{0.64}Sn_{0.36}$ electrodes provided a specific capacity of about 800 mA h g^{-1} in this potential range. The voltage profile of a-$Si_{0.64}Sn_{0.36}$ in PVDF [Fig. 10(a)] is equivalent to that of a-$Si_{0.64}Sn_{0.36}$ in TETA-crosslinked BRE-7131X [Fig. 10(b)]. This shows that the BRE-7131X polymer does not contribute to any unwanted side reactions in the cell.

Figure 11 shows the specific capacity (charge capacity) of both cells as a function of charge/discharge cycle number. The specific capacity of the a-$Si_{0.64}Sn_{0.36}$ electrode incorporating the PVDF binder decreases quickly upon the cycle number. It is our long-term goal to improve the capacity retention of a-$Si_{0.64}Sn_{0.36}$ using an elastomeric binder system. When the proposed elastomeric binder was used to replace the PVDF binder, the capacity retention of a-$Si_{0.64}Sn_{0.36}$ electrode was significantly improved. A reversible capacity of 800 mAh g^{-1} was maintained over 30 cycles.

CONCLUSIONS

Bisphenol-based and TETA-based crosslinking recipes were used to crosslink PVDF–TFE–P as a potential polymeric binder for lithium-ion batteries. The mechanical and electrical properties of crosslinked PVDF–TFE–P and PVDF–TFE–P/carbon black composites were evaluated after swelling in the liquid solvent EC/DEC (1 : 2 by volume).

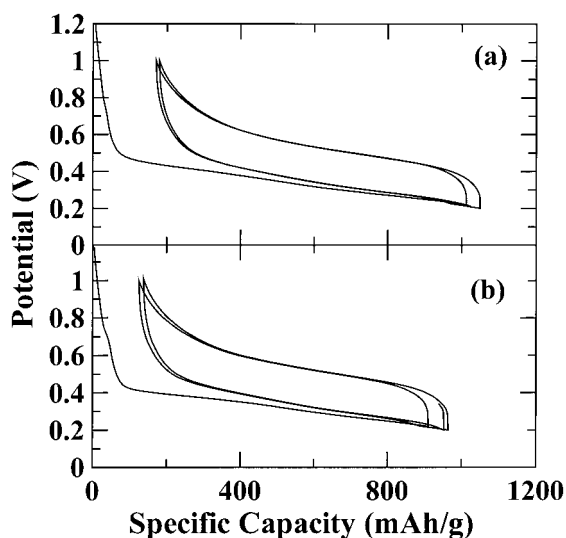Both bisphenol and TETA can successfully introduce a controlled degree of crosslinking in the terpoly-

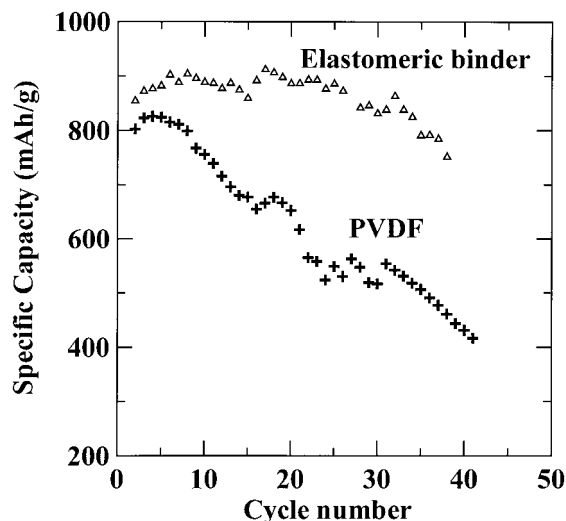**Figure 11** Specific capacity versus cycle number for cells with electrodes of a-$Si_{0.64}Sn_{0.36}$ showing the effect of the binder system. Both cells were first discharged to 0.22 V and then cycled between 0.2 and 1.0 V at a rate of 60 mA/g. The mass of a-$Si_{064}Sn_{0.36}$ per unit area is 5.67 and 5.55 mg/cm^2 for PVDF and PVDF–TFE–P, respectively.

mer PVDF–TFE–P and improve the mechanical properties of the polymer and the polymer/carbon composites. The TETA-crosslinked PVDF–TFE–P/carbon composites have better mechanical properties and higher reversibility than those crosslinked by bisphenol.

The addition of TETA was shown to have little or no effect on the electrical properties of carbon black–filled PVDF–TFE–P films. Therefore, we believe that the electrical properties of a particular electrode formulation using the TETA recipe will remain unaffected, whereas the mechanical properties can be tuned by changing the amount of crosslinking. Furthermore, the crosslinked polymer does not become brittle in typical solvents used in lithium battery electrolytes, so we believe that this highly extensible binder system may be useful for electrode materials that show large volumetric changes during charge/discharge cycling. The electrochemical characterization of a-$Si_{0.64}Sn_{0.36}$ clearly illustrated the superiority of the elastomeric binder over the conventional PVDF binder.

Figure 10 Voltage versus specific capacity for cells with electrodes of a-$Si_{0.64}Sn_{0.36}$ in (a) PVDF and (b) TETA-crosslinked BRE-7131X. Both cells were first discharged to 0.22 V and then cycled between 0.2 and 1.0 V at a rate of 60 mA/g. The mass of a-$Si_{064}Sn_{0.36}$ per unit area is (a) 5.67 mg/cm^2 and (b) 5.55 mg/cm^2.

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