Journal of Power Sources 195 (2010) 362–366

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Conductive ceramic coating on polyacrylonitrile–vinyl chloride (modacrylic) discontinuous fibers via electroless deposition

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ARTICLE INFO

Article history:
Received 25 June 2009
Received in revised form 5 July 2009
Accepted 6 July 2009
Available online 29 July 2009

Keywords:
Electroless deposition
Lead dioxide
Lead-acid battery
Modacrylic
Active material
Additive

ABSTRACT

Lead dioxide has electrical conductivity that is comparable to that of some of the metals. As a result like copper and nickel, lead dioxide can be deposited on non-conducting materials like polymers and ceramics using spontaneous and low cost deposition technique such as electroless deposition. This paper deals with development of conductive modacrylic fibers by coating them with lead dioxide via electroless deposition. The fibers so obtained will be used as additive in the lead-acid battery to improve its life and specific energy.

1. Introduction

Despite the amount of work done in the field of alternative electrochemical systems, the lead-acid battery is still the preferred choice of batteries to be used in plug-in hybrid vehicles (PHEVs) because of its low manufacturing cost. However, there are some disadvantages associated with the lead-acid battery [1]. During discharging of the battery, the lead dioxide in the positive plate is converted to lead sulfate. The lead sulfate is an insulator which creates a protective coating on the lead dioxide. This decreases the utilization of the battery, which is typically around 30%. The un-reacted material is undesirable, as it decreases the energy-to-weight and power-to-weight ratios of the battery. According to the recent studies based on conductivity model it has been successfully demonstrated that the utilization can be improved with small, conductive additives whereas large non-conductive additives do not significantly reduce utilization until a large volume percentage is used [2–6]. Also, the plates that constitutes the lead-acid battery, increase in size as the active material forms lead sulfate by using sulfate from sulfuric acid during discharge and decrease as they give up the sulfate during charging. This causes the plates to gradually shed the active material. Fibers such as modacrylic fibers which typically contain acrylonitrile and vinyl chloride offer mechanical reinforcement to the lead oxide paste on the grid of battery plate, there by reducing active material shredding and preventing premature failure of the battery. Moreover modacrylic fibers are non-biodegradable and are resistant to most organic solvents, oxidizing agents and sulfuric acid. Besides maintaining the mechanical integrity of the battery plates, enhancing the conductivity of modacrylic fibers by coating them with conducting oxide can increase the active utilization of the battery [7].

Traditionally conductive coatings, metals or metal oxides can be deposited using one of the several physical methods such as sputtering, vacuum evaporation, electron beam deposition, etc. [8]. Among the chemical techniques, anodic oxidation of metal ions is by far the most well known technique used to deposit metals. This technique has also been used to deposit oxides such as Tl_2O_3 and MnO_2 [9–10]. As far as deposition of lead dioxide using this technique is concerned, there is a general belief that electrodeposition leads to deposition of β-PbO_2 [11]. Some of the recent studies indicate the occurrence of α-PbO_2 alongside β-PbO_2 [12]. Electroless deposition is yet another chemical deposition method where deposition is carried out in the absence of external power source. There are different mechanisms underlying electroless deposition. In electroless deposition that proceeds by autocatalytic process, under the action of external reducing agent metals/metal oxide to be deposited serves as a catalyst. During electroless deposition that occurs via galvanic displacement, the electrons required for reduction are provided by

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doi:10.1016/j.jpowsour.2009.07.010

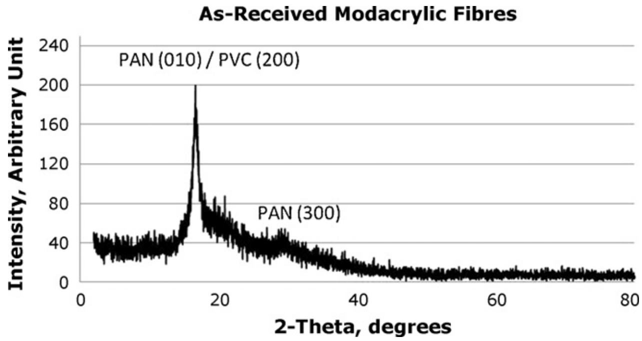

Fig. 1. X-ray diffraction pattern of as-received modacrylic fibers.

the substrate itself. Electroless deposition is often used to deposit copper and nickel. This technique can also be extended to metal oxides provided they are electrically conducting. Among the different oxides, lead dioxide is highly conducting and its conductivity is comparable to the conductivity of many metals. Hence electroless deposition serves as a viable and very useful alternative to deposit lead dioxide on non-conducting fiber such as modacrylic.

The objective of this study is therefore to develop conducting modacrylic fibers by coating them with lead dioxide via electroless deposition technique. The lead-acid battery designed using conducting modacrylic fiber additives is not only likely to last longer but will also possess higher specific energy.

2. Experimental details

In the present study, commercially available modacrylic fibers were used. Other materials used included lead acetate, ammonium acetate and potassium persulfate. Bath for electroless deposition was prepared by heating 12 ml of 0.8 M lead acetate solution, to which 15 ml of 3 M ammonium acetate and 10 ml of 0.2 M potassium persulfate solution was added. pH of the electroless deposition bath was maintained in the range of 10–12 using ammonia solution. The fibers to be coated were placed in the bath and the temperature of the bath was raised to 80 °C. Deposition was carried out for 30 min. The modacrylic fibers coated with lead dioxide were then rinsed with de-ionized water.

PbO_2 film deposited on modacrylic fibers was studied using Philips X-ray diffractometer (XRD) with Cu K_α radiation. PbO_2 coated modacrylic fibers were also studied for their surface morphology under Amray 1830 scanning electron microscope.

The Fourier transform infrared spectrum of as-received and lead dioxide coated modacrylic fibers samples were collected using Thermo Nicollet FTIR spectrometer.

3. Results and discussion

Modacrylic is a copolymer of acrylonitrile and vinyl chloride and typically contains 35–85% acrylonitrile. Fig. 1 is a X-ray diffraction pattern of as-received modacrylic fibers. The prominent feature of X-ray diffraction pattern of modacrylic fibers is a broad peak that appears at two theta values of 16–17° and a slight inflection at 23°, Fig. 1. While latter can be assigned to (3 0 0) crystallographic planes of polyacrylonitrile, the broad peak is probably due to (0 1 0) PAN crystallographic planes or (2 0 0) PVC crystallographic planes [12–13].

The as-received modacrylic fiber has fairly uniform diameter as can be seen from Fig. 2 which is a scanning electron micrograph of the as-received modacrylic fiber.

The modacrylic fibers when coated with lead dioxide via electroless deposition technique for half an hour also has uniform fiber diameter, Fig. 3. However, on the coated fiber surface apart from the uniform coating of lead dioxide there also appear well-defined crystals of lead dioxide, Fig. 3a. These crystals that grow from the electroless bath during the deposition process adhere very well to the fiber surface. Multi-faceted crystals of lead dioxide that grow alongside smooth coating also vary in size. There some crystals that are 5 μm in size while many others are close to 1 μm, Fig. 3b. Barring a few exposed patches, the modacrylic fiber surface appears to be completely covered with lead dioxide crystals. This kind of morphology of the coated fiber is likely to provide additional electrical conductivity along the fiber length.

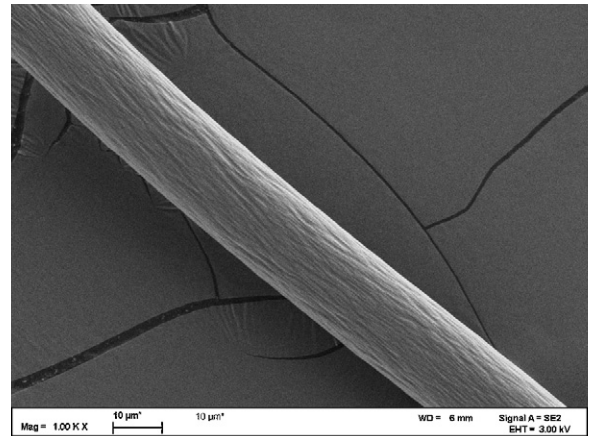

Fig. 2. Scanning electron micrograph of as-received modacrylic fiber.

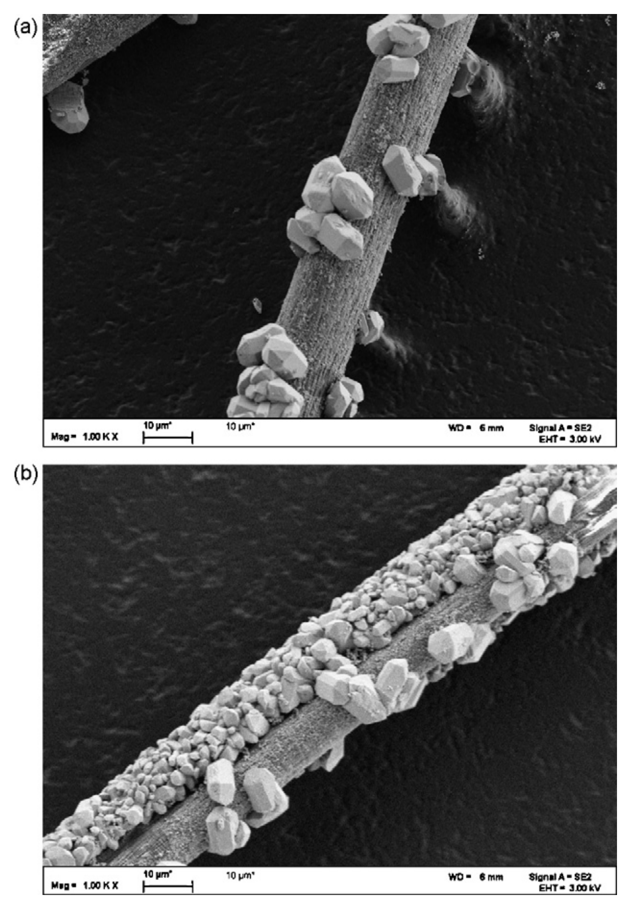

Fig. 3. Scanning electron micrograph of modacrylic fiber coated with lead dioxide.

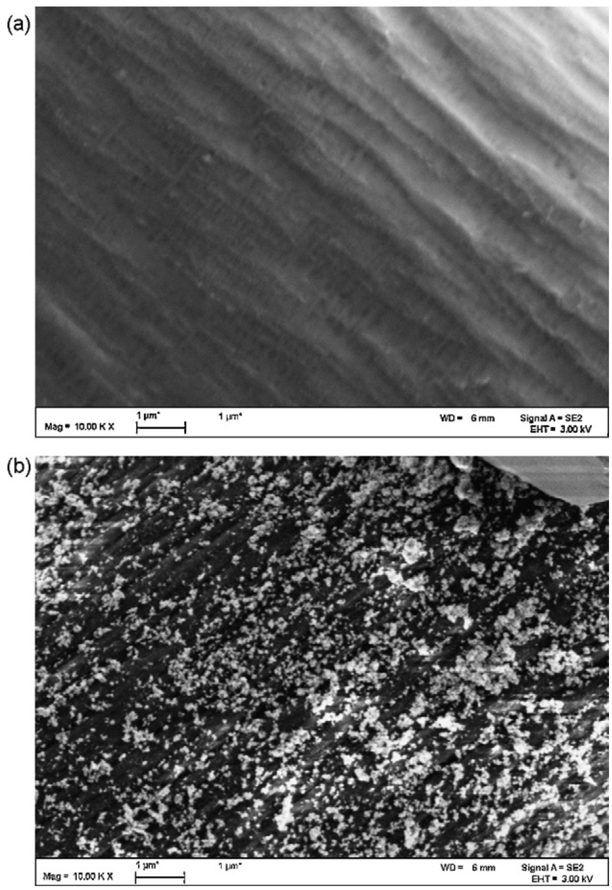

Fig. 4. Scanning electron micrograph of section of (a) as-received modacrylic fiber and (b) modacrylic fiber coated with lead dioxide.

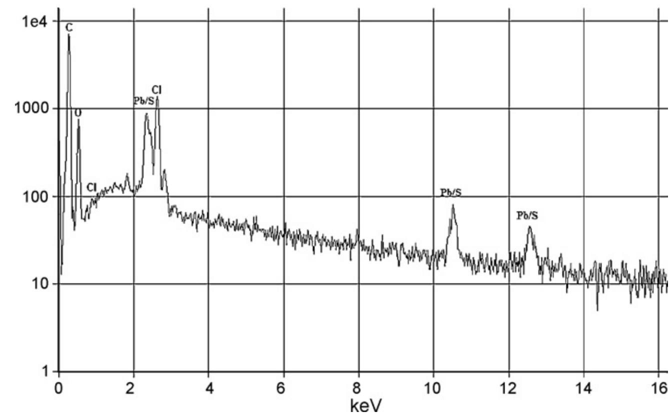

Fig. 5. EDAX spectra of lead dioxide coated modacrylic fiber.

Fig. 4 is high magnification scanning electron micrograph of section of as-received modacrylic fiber and lead dioxide coated modacrylic fiber. The surface of the as-received modacrylic fiber shows some amount of texture, Fig. 4a. This texture is probably caused during the melt spinning process. As far as lead dioxide coating on modacrylic fiber is concerned, what appears as a smooth coating is in reality made up of lead dioxide crystals with varying sizes, Fig. 4b. Many of the lead dioxide particles are less than 100 nm in size. Finer crystals of lead dioxide on the coated modacrylic fiber surface can be better resolved using transmission electron microscopy. Also, in certain regions of coated fiber surface the microscopic crystals appear as agglomerates that are not fully interconnected, Fig. 4b. This is likely to lower the electrical conductivity of the coated fiber. The morphology of the lead dioxide coated fiber surface can be improved by optimizing the bath composition and other deposition parameters such as pH, bath temperature and deposition time.

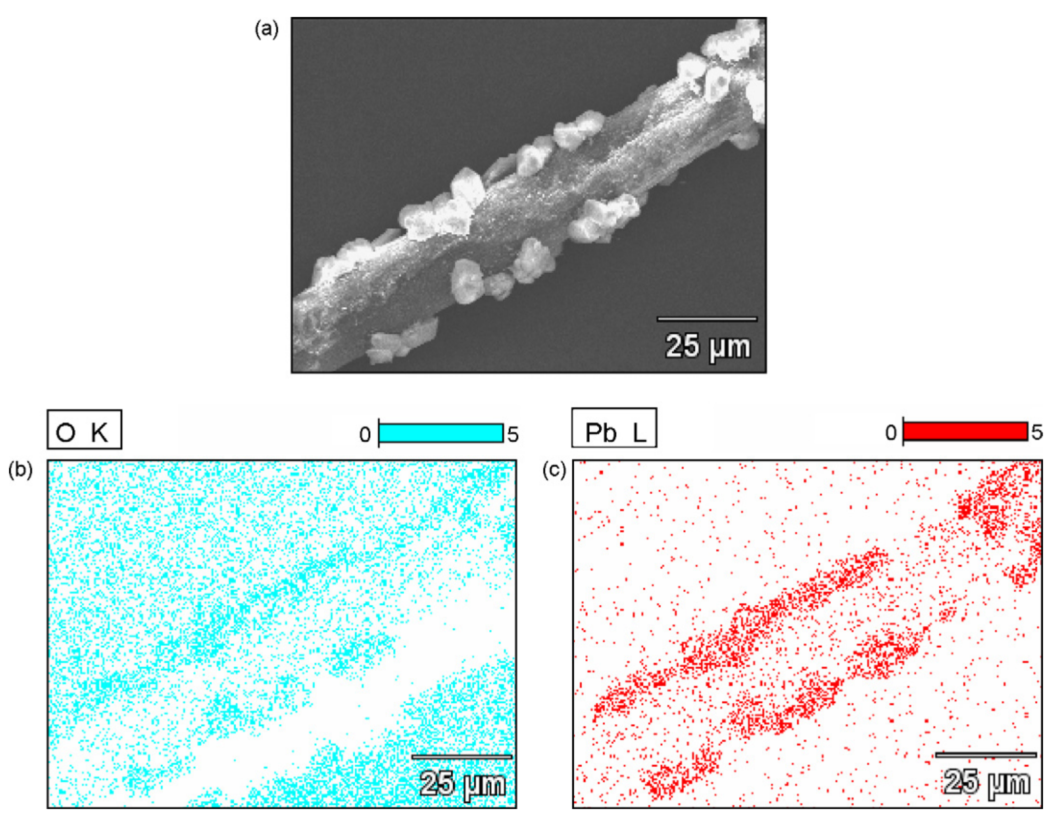

Fig. 6. (a) SEM image of a lead dioxide coated modacrylic fiber, (b) oxygen mapping, and (c) lead mapping.

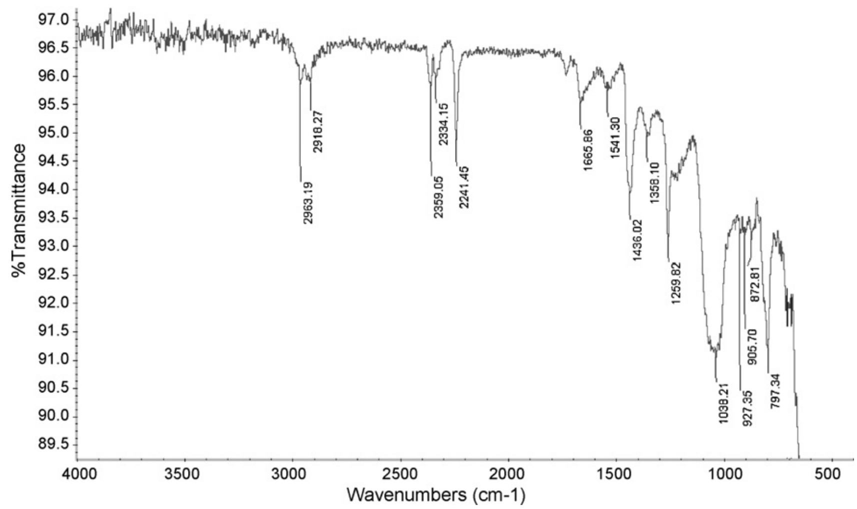

Fig. 7. FTIR spectrum of as-received modacrylic fibers.

Quantitative X-ray microanalysis performed using EDAX on lead dioxide coated modacrylic fiber indicate presence of chlorine, lead and oxygen, Fig. 5. EDAX fails to separate overlapping Pb and S lines. Using wave length dispersive technique it is possible to get better idea about elemental distribution on the coated fiber surface.

Fig. 6 shows scanning electron micrograph of the lead dioxide coated modacrylic fiber as well as elemental mapping performed on the fiber surface. The micrograph (Fig. 6a) shows the lead dioxide crystals that grow on the lead dioxide coated modacrylic fiber surface. Elemental mapping was performed on the lead dioxide coated modacrylic fiber surface to get an idea about the spatial distribution of oxygen and lead on the fiber surface, Fig. 6b and c. The mapping results indicate segregation of lead and oxygen atoms in the regions where the lead dioxide crystals grow. In the other regions on the surface of the coated modacrylic fiber the distribution of lead and oxygen is uniform.

To get a better understanding of the chemistry of the coated acrylic fiber, modacrylic fibers both as-received and coated were subjected to Fourier transform infrared (FTIR) spectroscopy. Infrared beams can penetrate all but the thickest of coatings, so that a transmittance spectrum of a coated fiber is usually a composite spectrum of the substrate (fiber) and the coating. Fig. 7 is the FTIR spectrum of as-received modacrylic fiber. The most prominent feature of this spectrum is C≡N stretching band that appears at 2245 cm^{-1}. IR bands at 1440 cm^{-1} represents C–H bending, and 1260, 1325, and 2964 cm^{-1} are due to C–H stretching. Most of the bands that appeared in the FTIR spectra of the as-received modacrylic fiber were absent in the FTIR spectra of the lead dioxide coated modacrylic fibers. Normally, lead dioxide shows IR peak in the region of 5200 cm^{-1}. Because this was beyond the range of the equipment, the FTIR spectrum of the lead dioxide coated modacrylic fiber failed to show the presence of lead dioxide.

As mentioned earlier, high electrical conductivity of lead dioxide is what makes the electroless deposition of lead dioxide on modacrylic fibers feasible. And because both the allotropic forms of lead dioxide, namely alpha and beta have comparable electrical conductivity, the resulting coating is likely to contain both the phases of lead dioxide. Fig. 8 is X-ray diffraction pattern of lead dioxide coated modacrylic fibers showing different phases formed on the fiber surface during the coating process. Similar patterns obtained using slow scan rate can potentially be used to perform quantitative analysis of the different phases.

As predicted both the alpha form (Scrutinyite) and the beta form (Platternite) of lead dioxide appear in the surface of the coated fiber, Fig. 8. These phases of lead dioxide are formed as per the following reaction

$$Pb^{2+} + 2H_2O \rightarrow (\alpha/\beta)\text{-}PbO_2 + 4H^+ + 2e^-$$

$$S_2O_8{}^{2-} + 2e^- \rightarrow 2SO_4{}^{2-}$$

$$Pb^{2+} + S_2O_8{}^{2-} + 2H_2O \rightarrow (\alpha/\beta)\text{-}PbO_2 + 4H^+ + 2SO_4{}^{2-}$$

Non-conducting PbO (Massicot) also appears in the coating along with lead dioxide, Fig. 8. PbO is formed probably due to the incomplete oxidation of lead ions as indicated by the following reaction:

$$Pb^{2+} + S_2O_8{}^{2-} + H_2O \rightarrow PbO + 2H^+ + 2SO_4{}^{2-}$$

Another prominent phase that is formed during the electroless deposition is lead oxide sulfate, Fig. 8. Normally lead oxide sulfate is formed by melting together PbO and $PbSO_4$. The composition of the lead oxide sulfate depends on the ratio of PbO and $PbSO_4$ [14]. Accordingly some of the lead oxide sulfates that have been reported include $Pb_2O(SO_4)$, $Pb_3O_2(SO_4)$, $Pb_4O_3(SO_4)$ and $Pb_5O_4(SO_4)$. These oxide sulfates of lead are also formed using hydrothermal methods [15].

$$4Pb^{2+} + 3H_2O \rightarrow 3PbO + 6H^+$$

$$S_2O_8{}^{2-} + Pb^{2+} \rightarrow PbSO_4$$

$$4Pb^{2+} + S_2O_8{}^{2-} + H_2O \rightarrow 3PbO{\cdot}PbSO_4\,(\text{lead oxide sulfate}) + 6H^+$$

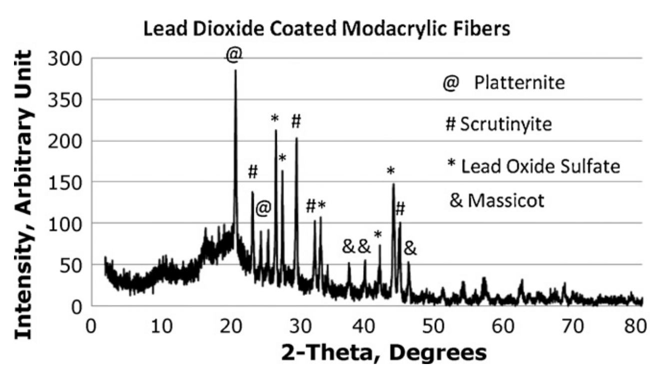

Fig. 8. X-ray diffraction pattern of lead dioxide coated modacrylic fibers.

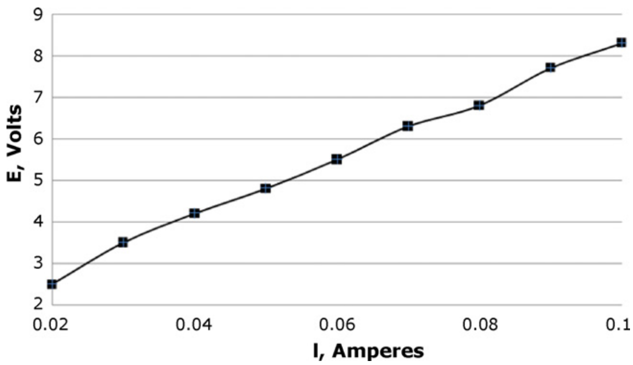

Fig. 9. Plot of current vs. voltage for the PbO_2 film deposited on glass slide.

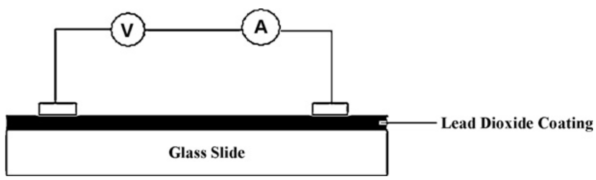

Fig. 10. Schematic of two probe setup used for studying current–voltage characteristic of PbO_2 film coated on glass slide.

Lead oxide (PbO) and lead oxide sulfate (Pb_5O_4 SO_4) are electrically non-conducting. Therefore, their occurrence is likely to adversely affect the electrical conductivity of the coated modacrylic fibers.

Fig. 9 shows the current voltage characteristics of PbO_2 film deposited on glass slide using identical electroless deposition conditions used to coat modacrylic fiber. Current–voltage curve was generated using two probe method, the schematic of which is shown in Fig. 10. Using the current vs. voltage curve, the specific resistance computed for the PbO_2 film was found to be $350 \times 10^{-8}\ \Omega$ m. The specific resistance of PbO_2 film is fairly high compared to that of silver which has a specific resistance of $1.5 \times 10^{-8}\ \Omega$-m but is comparable to specific resistance of manganese with specific resistance value of $135 \times 10^{-8}\ \Omega$-m.

4. Conclusion

Modacrylic fibers were successfully coated with conductive lead dioxide using electroless deposition technique. These coated modacrylic fibers will be used as additive in lead-acid battery to improve its life and specific energy.

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