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Substrate materials for bipolar lead/acid batteries

Wen-Hong Kao *

Advanced Battery Research, Johnson Controls Battery Group, Inc., MS B-5, 5757 N. Green Bay Avenue, Milwaukee, WI 53201 USA

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Abstract

Attempting to develop a composite substrate for a bipolar lead/acid battery, more than 120 ceramic materials were screened. About 60 of them having a conductivity greater than 10 Ω^{-1} cm^{-1} and cost less than US$ 1/g were tested. Test methods and devices were developed to examine the chemical and electrochemical stability of the filler materials, oxygen and hydrogen overpotential, and porosity of a composite substrate made of polyethylene with dispersion of the conductive filler. Very few of the ceramic materials we tested possess the desired stability, high oxygen/hydrogen overpotential and imperviousness to the acid electrolyte. Silicides of Ti, Nb and Ta appear to be acceptable fillers for plastic composite substrates. These composite substrates, however, lacked of paste adhesion and were heavy. The properties of these conductive fillers and directions for improvement in the development of a bipolar substrate are discussed. © 1998 Elsevier Science S.A.

Keywords: Lead/acid batteries; Bipolar configuration; Ceramic materials

1. Introduction

A battery with a bipolar configuration is known to be advantageous over the conventional monopolar configuration in terms of power output. In a conventional battery, current generated by active materials travels to a current collector and through an outer circuit to reach the next cell. In the bipolar configuration, active materials of opposite polarities are placed on the two surfaces of a bipolar substrate. Current can thus flow through the substrate to the next cell. Because of a much shorter electrical path, power loss due to ohmic drop in the circuit is minimized. The volume of the battery is reduced due to elimination of the outer circuit materials such as straps, posts and tabs.

In a bipolar lead/acid battery, the role of the substrate is paramount. The substrate serves as an intercell connection and as a support to active materials. It provides seals between and isolates electrolyte in individual cells. It must retain its electrical conductivity in the corrosive lead/acid environment and break communication of electrolyte in adjacent cells through the service life of the battery. Furthermore, it may not participate in or provide alternative routes to the battery reactions. To satisfy these requirements, a substrate must be electrically conductive, insoluble in sulfuric acid, stable in the potential window of the battery, having high oxygen and hydrogen overpotentials, inert to battery reactions, impervious to the electrolyte, having good adhesion to the battery active materials, and easy to process and seal to the battery case. Success in developing a bipolar substrate relies heavily on the identification of a material which possesses all of the above properties.

Kapitza and Heath [1] patented a bipolar lead/acid battery in the early 1920s. Similar battery configurations for other systems were also suggested. Lead sheet was used as the substrate in this early bipolar lead/acid battery. The active materials were formed on the substrate using a Planté process. The sheets were stacked between U-shaped rubber gaskets. This battery could deliver a current density between 2 and 5 A/cm^2 for a few milliseconds with a power density of around 2 kW/l. There was no significant progress in the development of a bipolar lead/acid battery thereafter until Biddick and Nelson [2] modified this battery in the late 1960s by providing seals and vents without other changes in the battery features. The problems in the Kapitza-type bipolar lead/acid battery include sealing, substrate corrosion, and lack of capacity. From the 1960s on, pastes of active materials have been used to replace the Planté process to improve battery capacity. Modification on the lead sheet substrate or uses

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* Corresponding author. Tel.: +1 (414) 228 32 51; Fax: +1 (414) 228 20 08; e-mail: Wen-Hong.Kao@JCI.COM.

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of other materials have been studied to improve sealing and to retard substrate corrosion. For example, a Russian patent [3] discloses a substrate of lead sheet with a glue-on titanium sheet using conductive adhesives. Another important development is the invention of a plastic composite, such as a carbon plastic.

In their development of a bipolar lead/acid battery for the Environmental Protection Agency, Biddick et al. [4] considered gold-plated titanium and conductive plastics as a bipolar substrate. The gold-plated titanium was given up in an early stage of their program due to difficulties in achieving a pore-free adherent gold plate and working the titanium into a usable configuration. Commercially available conductive epoxides and thermoplastics with fillers such as carbon, graphite, copper, and silver were eliminated because they reacted with the cell environment. Vitreous carbon from Beckwith Carbon (CA, USA) however, was identified to be a suitable filler. Their efforts were therefore focused on fabrication and evaluation of various plastics filled with finely divided vitreous carbon powder. As a result, an epoxy-vitreous carbon substrate was successfully fabricated. However, their attempt to paste and form active materials on this substrate failed because of interfacial corrosion on the positive side of the substrate. In the mean time, some other plastic materials suitable for the substrate, such as a polyvinylidene fluoride sold by Pennwalt under the name Kynar® and NORYL-731® polyphenylene oxide from General Electric, were identified [5]. Some similar carbon/polymer composites were developed by Yardney International [6] and Exxon [7], using Vulcan XC-72 carbon as the filler, for zinc/bromine batteries.

Tin dioxide is known to be conductive and stable in dilute sulfuric acid. A tin dioxide coated glass electrode, known as an optically transparent electrode (OTE), has been used as an indicator to study electrochemical systems since 1964 [8]. A number of processes for coating tin dioxide on glass and ceramic bodies of various shapes has been patented [9]. Doped tin dioxide was a focus of substrate development in Jet Propulsion Laboratory (JPL) and their subcontractor ENSCI, in the 1980s. Initially, tin dioxide coated glass fibers were added to the positive paste to improve plate conductivity, formation, and cycle life [10]. This material was also dispersed into polypropylene which was then laminated with a lead sheet to form a monopolar electrode [11]. The plastic composite was porous and therefore this monopolar electrode could not be converted to a bipolar substrate. Later development involved lamination of the SnO_2/glass fiber dispersed electrode with carbon plastic [12], uses of fluorine-doped SnO_2 with polymeric resin having increases polarity relative to polypropylene [13], uses of coupling agents such as silane and titanates [13], and surface conditioning by wetting agents or plasma oxidation with ozone to render the substrate more wettable by the active materials [14].

Titanium was one metal in consideration for a bipolar substrate. However, titanium passivates at the positive potential of a lead/acid battery and can dissolve at a discharging potential. Extra protection of the metal, such as plating with gold or lead, or laminating with lead or conductive plastic [15] is needed. Such protective coatings, however, add weight and cost. The International Nickel Company (INCO) discovered one way to modify titanium for lead/acid batteries [16]. They impregnated lead into a sintered electrode of titanium powder or other valve metals. This electrode was used by ESB Technology, now Exide Management and Technology Company, in their development of a bipolar lead/acid battery for electric vehicle propulsion for the Department of Energy.

While difficulties were experienced in developing a true-bipolar substrate, alternative configurations were investigated. Terms such as 'quasi-bipolar' and 'folded bipolar were used to describe the alternative configurations. In the patent assigned to Tyco Laboratories of Massachusetts [17], a bipolar plate was described as containing a rectangular polycarbonate base plate with a straight horizontally extending hole adjacent to its top end. The lower edge of the hole had a plurality of narrow, evenly spaced slots. Lead strips were folded over the slots in the hole and secured onto the base plate with a rectangular polycarbonate grid containing evenly spaced horizontal struts or bars in parallel. A frame with a defined aperture was then disposed on the grid. In this design, the array of lead strips serves as the intercell connection and support of active materials. A wide top section of the grid and frame is bonded to the base plate to conceal the hole and to prevent acid leakage. The concerns, however, are corrosion of the lead strips and acid creep along the strips to short the adjacent cells. The Pulsar® battery developed by Dunlop Australia [18] possesses the concept of a quasi-bipolar plate in which an expanded metal grid of the so-called double width mesh extends from one division of the frame to the next division through a plastic partition. A quasi-bipolar design patented by CIT [19] is similar to the Tyco design in which lead strips covering a substrate are joined on the top or side of the substrate. In the design patented by Johnson Controls (JCI) [20], a non-conductive plastic substrate is die-cut to form two to three slots. Lead expanded metal is then folded at the slots. The slots are then heat sealed with plastic strips.

At JCI, we have been looking for a material as a filler in a plastic composite substrate for bipolar lead/acid batteries. Methods and procedures have been developed to screen the conductive fillers. Test devices are designed to evaluate the required properties mentioned earlier for each filler candidate. The methods include a digestion test to define the chemical stability of the filler in sulfuric acid, a polarization test simulating charging conditions for electrochemical stability of the substrate, cyclic voltammetry to define oxygen and hydrogen overpotentials, and a porosity test using a convertible three-/four-electrode system. Reported herein are results of this research.

2. Experimental

The filler candidates are tested for chemical stability, electrochemical stability, oxygen/hydrogen overpotential and porosity of its plastic composite, in that order. If a candidate fails in any stage, usually no further test is performed. This screening test is designed to quickly eliminate those inapplicable candidates. A filler candidate which passes the four-step screening test is made into a substrate to test paste adhesion and formation. If the results are positive, a battery is then built to test performance.

For chemical stability tests, 1 g of powder filler is dry mixed with 1 g of reagent-grade PbO_2 in a 250 ml Erlenmeyer flask. 50 ml of sulfuric acid of 1.305 specific gravity is added to the flask. The flask is sealed with a rubber stopper and either placed on benches at room temperature or immersed in a water bath at 40 or 60 °C for 7 to 9 days. In the case of high-temperature digestion, a plastic tubing running through a hole in the stopper connects the system to a water pool to provide the 'water seal'. This is to contain water vapor while maintaining the same atmospheric pressure in the system. After digestion, the solid is separated by filtering the mixture through a preweighed crucible. The solid is washed with 50 ml of water in three parts. The filtrate and washing liquid are saved and the volume is adjusted to 150 ml. This electrolyte is analyzed using inductively coupled plasma spectroscopy (ICPS) for the quantity of the parent material. The solid is dried in an oven at 90 °C for at least 12 h and then weighed and analyzed with X-ray diffractometry (XRD) for any possible changes in crystalline phases. The filler is considered a failure if it decomposes, loses more than 1% of weight or changes its crystal structure to a non-conductive state.

A one-compartment electrochemical cell is used for the electrochemical stability test. A working electrode substrate, about 1 cm × 2 cm, is immersed in a large quantity of sulfuric acid of 1.305 specific gravity with a lead spiral counter electrode and a reference electrode of Hg/Hg_2SO_4 in sulfuric acid of specific gravity 1.265. A platinum wire attached to the substrate with a conductive glue serves as the current lead. The wire is then epoxied to prevent exposure of the current lead to the electrolyte. A constant potential, about 1.5 V, is applied for a period of time varying from a few hours to several days. The sample electrode is then removed, washed thoroughly with deionized water, dried and measured for electrical resistivity using a four-point probe. Changes in electrical resistivity as a function of time are monitored. The electrode substrate is considered a failure if its electrical resistivity consistently increases with polar-ization time and the value becomes 10 Ω cm or higher after about three weeks in test. This value was chosen because computer simulations [21] indicated that the bipolar battery would lose its power advantages over the monopolar configuration if the substrate became too resistive.

The same device in the above test is used for cyclic voltammetry to determine the oxygen and hydrogen overpotentials. The potential is first scanned anodically from its rest potential to a value greater than 2 V versus the reference electrode and then back to 0 V. The switching potential is reduced if severe gassing is observed. The scan continues to about −1.5 V and then back to the initial rest potential for hydrogen overpotential. The onset potential of oxygen or hydrogen evolution is defined to be the foot potential of a rising current in the respective scan which is accompanied with gas evolution at the electrode surface. This onset potential is then compared with the reduction potential of PbO_2 which is about 1.25 V, or oxidation potential of Pb at about −0.9 V. An electrode substrate which generates gases within this potential window is considered unstable and would cause spontaneous self-discharge of the battery.

A dual-cell device shown in Fig. 1 is used to test porosity and the ionic conductivity through an electrode

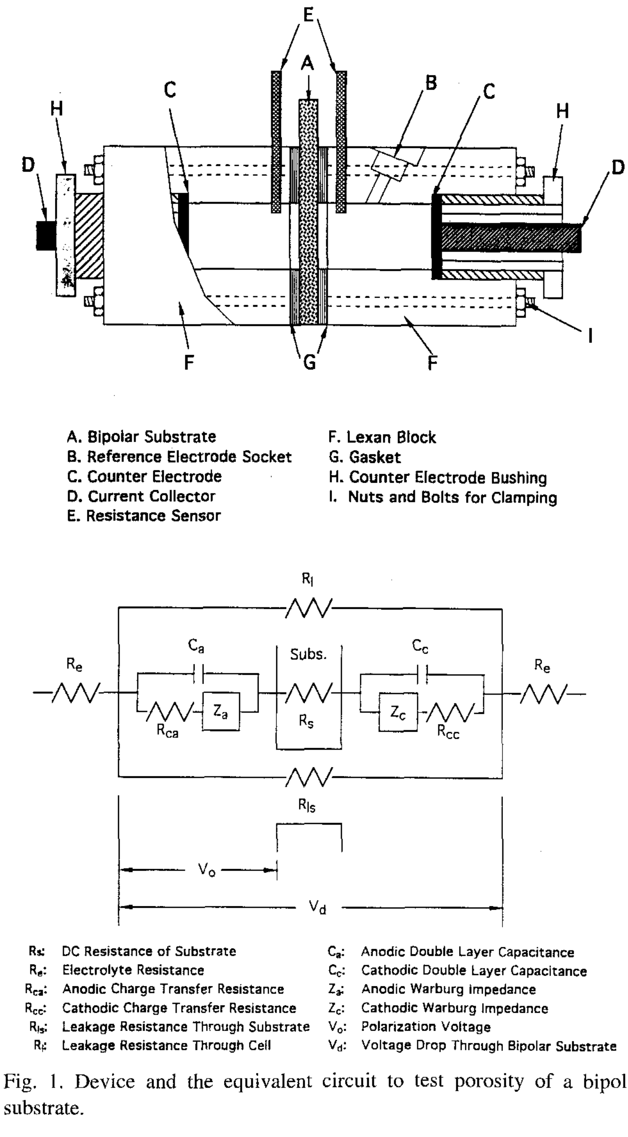

Fig. 1. Device and the equivalent circuit to test porosity of a bipolar substrate.

substrate. The equivalent circuit of the test device is also shown in Fig. 1. The concept of this test was originated from Attia of JPL and modified by the author. The working electrode substrate is sandwiched by the two cells with an opening about 11.4 cm^2. At first, a constant potential, about 1.35 V, is applied to the substrate across the reference electrode residing in one cell compartment and the current is monitored. After the current becomes stable, the working electrode lead is moved to the counter electrode, i.e. the fourth electrode, in the second cell compartment and the test is switched to the constant-current mode. Current flow through the working electrode is adjusted so that the voltage drop between the working and the reference electrode remains constant at 1.35 V. The current required to sustain the voltage drop is monitored and compared to the value from the three-electrode test. Two retractable tantalum wires positioned on the two sides of the substrate are used to measure the voltage drop across the substrate. The resistance across the substrate is then calculated with the compensation of the electrolyte resistance.

According to the circuit shown in Fig. 1, R_l is infinite if the cells are leak-proof. C_a and C_c are saturated under steady-state conditions. With constant V_o, the current generated under three-electrode polarization conditions is $I = V_o/(R_{ca} + Z_a)$. Under four-electrode polarization conditions, the total current would be the sum of the polarization current and the leakage current, i.e. $I_T = I + I' = V_o/(R_{ca} + Z_a) + V_d/Rt_{ls}$. If the substrate is non-porous, R_{ls} would be infinite and I' is equal to 0, i.e. $I_T = I$. If the substrate is porous, R_{ls} has a finite value and I' is greater than 0, i.e. $I_T > I$. Therefore, a current rise during the switch from the three-electrode polarization to the four-electrode polarization would suggest a porous substrate.

The majority of the materials we tested were purchased from Cerac Incorporated (Milwaukee, WI, USA). Some materials not available commercially were synthesized in house. PbO$_2$ reagents were purchased from Aldrich Chemical (Milwaukee, WI, USA). A substrate was formed by blending a filler into a melting plastic followed by compression under a pressure of about 5 ton/in^2. Electrolyte was prepared using battery-grade sulfuric acid and deionized water. XRD was performed using a Philips diffractometer with Cu Kα radiation. An EG&G PARC 173 potentiostat/galvanostat (Princeton, NJ, USA) and a PARC 175 Universal Programmer were used for potential/current control and cyclic voltammetry.

3. Results and discussion

Over 120 different ceramic materials were examined. About 60 of them which have an electrical conductivity greater than 10 Ω^{-1} cm^{-1} and cost less than US$ 1/g were tested. The results of the tests on some binary compounds are summarized in a matrix shown in Table 1. These compounds are grouped according to the family of the metals in the periodic table and their anionic counterparts. No quantitative values of the test results are given. Instead, the failure mode of each filler candidate is indicated. Also screened were composites having a perovskite structure, such as BaPbO$_3$, BaBiO$_3$, BaTiO$_3$, BaSnO$_3$, SrPbO$_3$, Ba$_x$Sr$_y$PbO$_3$ ($y \leq 0.1$, $x = 1 - y$), BaPb$_x$Sb$_y$O$_3$ ($y \leq 0.25$, $x = 1 - y$), BaPb$_x$Bi$_y$O$_3$ ($y \leq 0.35$, $x = 1 - y$), Na$_2$TiO$_3$, CaZrO$_3$ and LaCrO$_3$. Unfortunately, BaTiO$_3$, BaSnO$_3$, Na$_2$TiO$_3$, CaZrO$_3$ and LaCrO$_3$ decomposed readily and other composites either decomposed slowly or lost the dopant, i.e. Sb or Bi, in sulfuric acid.

Table 1
Results of screening tests

Elements	Borides	Carbides	Nitrides	Oxides	Silicides
IIIB			ScN [a]		
	LaB_6 [a]		LaN [a]		$LaSi_2$ [a]
IVB	TiB_2 [a]	TiC [a]	TiN [a]	TiO_x [a]	$TiSi_2$ [e]
					Ti_5Si_3 [e]
	ZrB_2 [a]	ZrC [a]	ZrN [a]		$ZrSi_2$ [a]
VB	VB_2 [a]	VC [a]	VN [a]		VSi_2 [a]
	NbB [b]	NbC [c]	NbN [b]		$NbSi_2$ [c]
	NbB_2 [b]				
	TaB_2 [b]	TaC [b]	TaN [b]		$TaSi_2$ [e]
	TaB [b]				Ta_5Si_3 [e]
VIB	CrB [a]	Cr_3C_2 [a]	CrN [a]		
	MoB [a]	Mo_2C [a]		MoO_2 [a]	$MoSi_2$ [a]
	W_2B_5 [b]	WC [c]		WO_x [b]	WSi_2 [b]
				ReO_3 [a]	
VIIB					$MnSi_2$ [b]
VIII					$CoSi_2$ [b]
					$NiSi_2$ [b]
IB					Cu_5Si [b]
IIIA		BC [a]		In_2O_3 [a]	
IVA		SiC [b]	Si_3N_4 [a]	SnO_2 [d]	

[a] Dissolves or decomposes in sulfuric acid.
[b] Unstable electrochemically, either decomposes or passivates.
[c] Low oxygen overpotential.
[d] High porosity in the substrate.
[e] Passes the screening test.

From Table 1, all the borides and nitrides tested, except TaN, are unstable chemically or electrochemically. Tantalum boride can be oxidized at around 1.0 V (Fig. 2). Some carbides such as NbC, TaC and WC pass the stability tests but the oxygen overpotential of these materials is low (examples in Fig. 2). Silicides of titanium, niobium and tantalum pass the stability test. Among them, the titanium and tantalum silicides also show high oxygen overpotential (Fig. 2) and can be made into a non-porous substrate. Oxygen overpotential of NbSi is marginal. Manganese silicide, although showing good oxygen potential (Fig. 2), can be oxidized and then dissolved into acid.

Some materials may appear to be stable, based on weight loss in the digestion test. These materials, although not dissolving or decomposing during digestion, may passivate or change their stoichiometry. Five filler materials passing the initial chemical stability test were made into

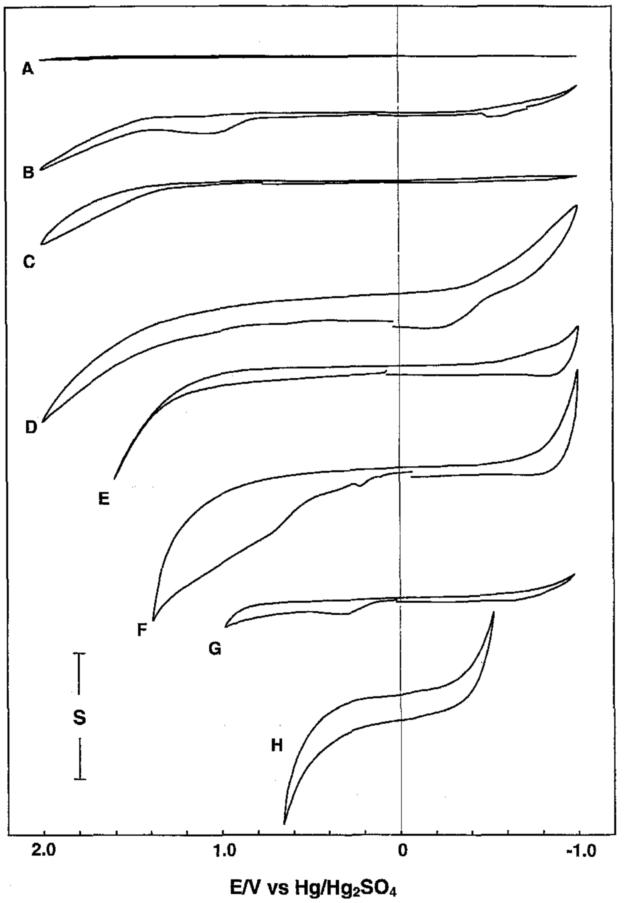

Fig. 2. Cyclic voltammograms for PE composites of: (A) $TaSi_2$; (B) TaB; (C) $MnSi_2$; (D) $TiSi_2$; (E) $NbSi_2$; (F) NbC; (G) TaC, and (H) WC in sulfuric acid of gravity 1.265. $S = 2$ mA/cm^2, and scan rate = 10 mV/s.

substrates and tested for electrochemical stability. The changes of substrate resistance as a function of digestion time are illustrated in Fig. 3. From Fig. 3, the rate of increase in the resistance of the substrates filled with silicides and SnO_2 is relatively slow. TaN is eliminated from the list of candidates because of the rapid rise in substrate resistance.

SnO_2 has a high oxygen overpotential but the stoichiometric SnO_2 crystal is not conductive. The conductivity of SnO_2 comes from structural defects caused by low-valent Sn metal or dopants, such as antimony and fluorine [13] in the lattice. Prolonged exposure of SnO_2 in acid under a positive potential usually results in passivation due to conversion of low valent tin or loss of the dopants. As shown in Fig. 3, the resistance through the thickness of an SnO_2/polyethylene (PE) substrate increases by a factor of 5 after 350 h of polarization. On the other hand, it is very difficult to make a non-porous SnO_2/PE composite. A SnO_2/PE substrate subject to polarization test quadrupled the current (Fig. 4) when the system was switched from a three-electrode to a four-electrode, although the porosity estimated from the ionic resistance through the substrate was less than 0.2%. The increase in resistance through the substrate during this test is similar to that observed in the electrochemical stability test.

Another conductive material which appears to be stable is tungsten suboxide, WO_x ($2.6 \leq x \leq 2.9$). This material does not lose weight or decompose during the digestion test. However, the stoichiometry gradually changes with time and approaches WO_3, which is an insulator. Like SnO_2, it is very difficult to make a non-porous WO_x/PE

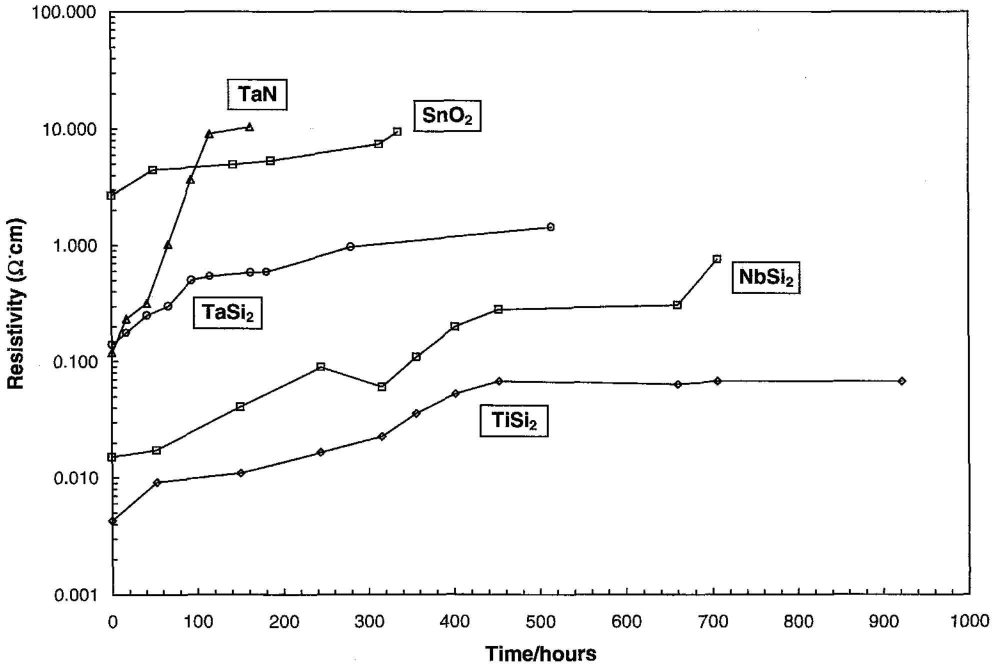

Fig. 3. Resistivity of PE composites with TaN, SnO_2, $TaSi_x$, $NbSi_2$ and $TiSi_2$ as a function of polarization time at 1.35 V. The loading is 30% for SnO_2, 40% for $TaSi_2$, and 60% for others.

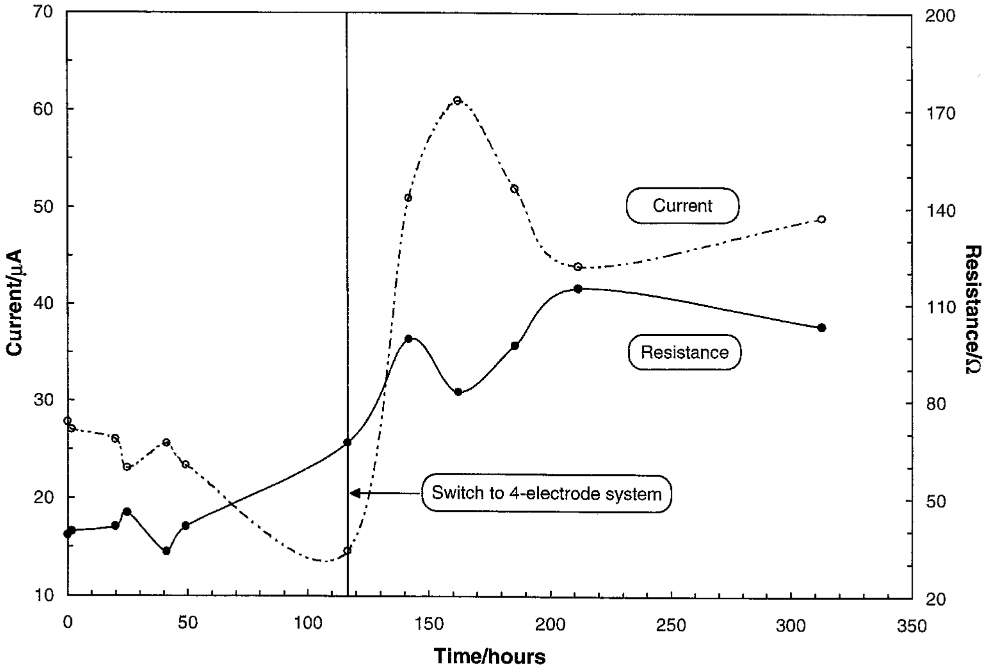

Fig. 4. Porosity test of a SnO_2/PE (30% by volume) substrate.

substrate. One idea explored was to laminate the WO_x substrate with a known non-porous composite, such as a carbon plastic. The results of the porosity test (Fig. 5) show no change in current when the system is switched from a three-electrode to a four-electrode. The polarization current stays the same through the test but the resistance through the substrate steadily increases after about 200 h. The test was terminated after 1000 h and the cross section of the substrate was examined. As shown in Fig. 6, voids were found at the interface of the WO_x substrate and the carbon plastic. It is known that carbon plastic is subject to oxidation under the test conditions. Apparently, acid penetrates through the WO_x layer, reaches the interface and oxidizes carbon during the test. Similar results would have occurred on a laminated SnO_2/carbon plastic substrate.

Based on the above results, the best candidates among

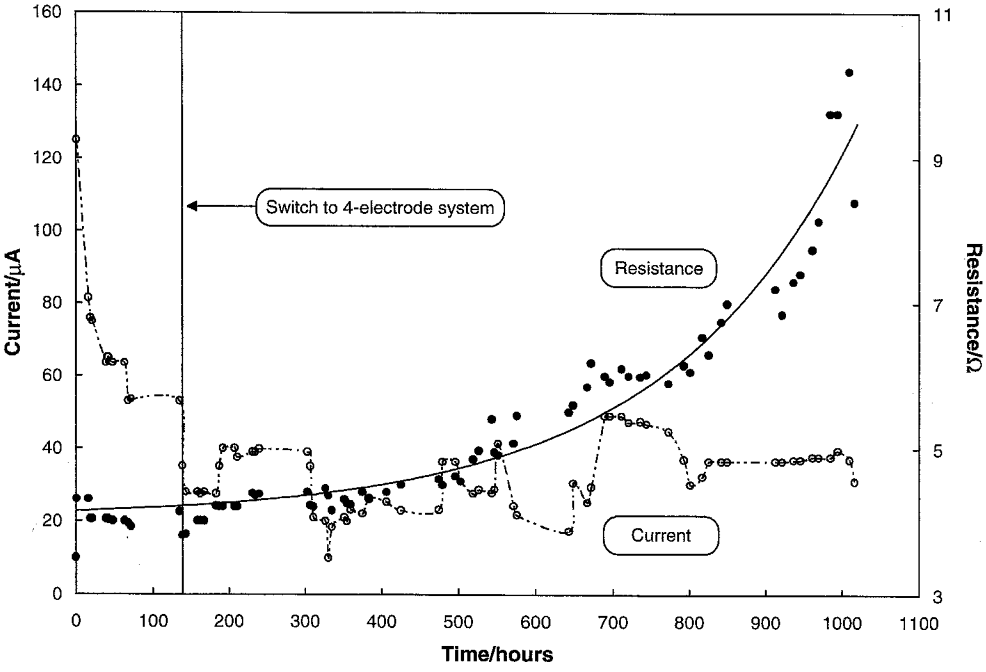

Fig. 5. Porosity test of a WO_x/PE (35% by volume) substrate laminated with carbon plastic.

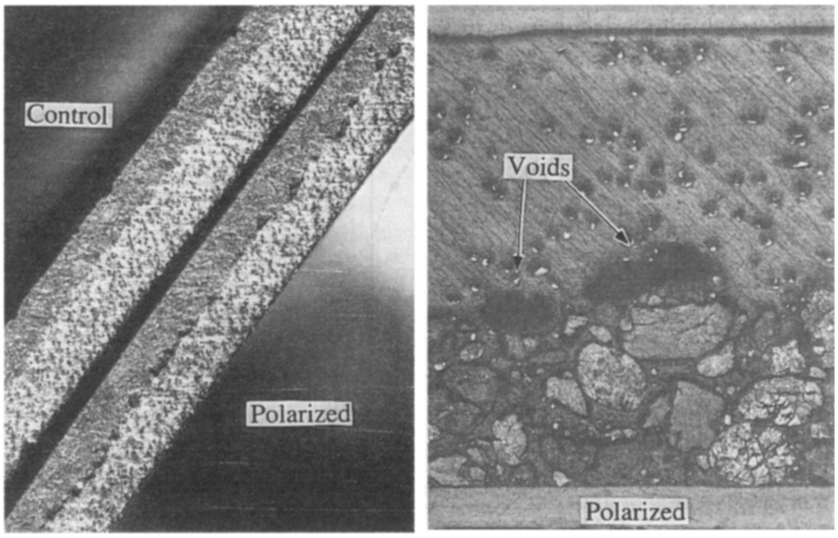

Fig. 6. Optical micrograph of the cross section of control and polarized WO_x–carbon plastic laminate substrate. The large round objects are WO_x particles. The small round objects are the tips of glass fibers in the carbon plastic.

the materials we have tested are $TiSi_2$ and $TaSi_x$. $NbSi_2$ may be acceptable. A $TiSi_2$/PE composite substrate with 60% by volume of the filler has a density about 2.82 g/cm^3, and conductivity about 233 Ω^{-1} cm^{-1} or resistivity about 0.0043 Ω cm. For comparison, the $TaSi_x$/PE and $NbSi_2$/PE substrate at the same loading level would yield 8.20 and 3.77 g/cm^3 density with 0.007 and 0.015 Ω cm resistivity, respectively. At 40% loading level, the density of the $TaSi_x$/PE substrate reduces to 4.22 g/cm^3 but the resistivity increases by a factor of 4 to 0.29 Ω cm. The resistivity of these substrates does increase if digested in acid, as shown in Fig. 3, due to slow decomposition of the compound and oxidation of the metal. From the extrapolation of the curve, it would take 940 days of continuous polarization at 1.35 V versus Hg/Hg_2SO_4 for the $TiSi_2$/PE substrate to reach 10 Ω cm, a bench mark where the bipolar battery would perform at the same level as a monopolar battery. Such stability is considered excellent for most applications of lead/acid batteries. In contrast, the polarization time required for $TaSi_x$ (40% by volume) and $NbSi_2$ (60% by volume) substrates to reach the bench mark would be 124 days and 87.5 days, respectively.

Concerns about the composite substrate include weight and paste adhesion. The substrates we have made for tests are about 500 μm thick. A thinner substrate becomes brittle and difficult to handle. At 50 mm, the area density is 143, 214 and 191 mg/cm^2 for 60% $TiSi_2$/PE, $TaSi_x$/PE and $NbSi_2$/PE substrate, respectively. These values are slightly lower than the density of a quasi-bipolar substrate [20], which is about 230 mg/cm^2, and a 200 μm thick lead foil (225 mg/cm^2). Considering the cost of materials and processing for the plastic composite, the plastic bipolar substrate may have a cost disadvantage comparing with the quasi-bipolar design or lead foil. One $TiSi_2$/PE was pasted with active materials but the active materials fell off after curing. Lacking paste adhesion is an apparent problem for plastic substrates. The adhesion was improved with heat impression of a lead expanded metal into the substrate to hold the paste. However, the formation failed due to heavy sulfation at the plastic/paste interface, suggesting lack of interaction between the plastic substrate and active materials. An interface to link the substrate and active materials, such as a lead foil or some sorts of chemical treatment to improve bonding between plastic and active materials, would be necessary. To find a cost effective interfacing method would be another tough challenge.

4. Conclusions

Very few of the ceramic materials screened possess desired properties to be applicable in a bipolar substrate for a lead/acid battery. Among the 120 candidates, silicides of Ti, Nb and Ta appear to be acceptable as fillers for the composite substrates. However, texture or lamination with a lead foil to interface the substrate and active materials is necessary to improve paste adhesion.

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