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Under potential deposition of lead onto carbon fibres for use in lead/acid battery applications

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An effective method of reducing the mass of a lead acid battery is to replace the lead with a less dense electrical conductor such as carbon. The application of a thin layer of lead onto the surface of carbon fibres can improve the electrical and mechanical properties of the bond between the fibre and battery active material. Under-potential deposition was used to apply a thin layer of lead onto carbon fibre tows. The efficiency of this process using a number of different electrolytes and voltage ranges was assessed. X-ray photoelectron spectroscopy and secondary ion mass spectroscopy were used to evaluate the deposition process. Lead was successfully deposited onto the surface of the fibres at a potential of approximately 262 mV using the electrolyte consisting of 0.1 M $HClO_4$ and 0.01 M $Pb(OAC)_2$. © *2002 Kluwer Academic Publishers*

1. Introduction

A substantial proportion of the total mass of a lead acid battery is the lead grid and the current connectors between cells. The mass of a battery is an important factor in transport applications such as aviation where additional weight can lead to increased fuel consumption. A logical approach to reduce the mass of a battery is to replace the lead with a less dense material. Carbon fibres are both lighter and stronger than lead and also have a reasonable stability in sulphuric acid electrolyte environments. Construction of a composite material consisting of carbon fibres dispersed within a lead matrix would be both lighter and stronger than pure lead. Improved mechanical properties would lead to smaller components reducing battery weight further. However when producing a fiber composite, properties are dependent on good bonding between fibre and matrix.

Coating carbon fibres with a stable mono-layer of lead would produce a surface which is more suitable for battery paste adhesion, or which could be used in the production of a composite. In this instance, the presence of a stable intermediate lead layer may aid wetting of the fibres by the matrix metal, either under rolling conditions, or as molten lead when used in squeeze casting. Improved wettability would improve the integrity of the composite and improve the mechanical properties.

Under-potential deposition (UPD) is an electrochemical technique, which can be used to deposit a metallic monolayer onto the surface of an electrode, at potentials more positive than the Nernstian reversible potential [1]. Stable multiple layers of the deposition metal can however be obtained, using cyclic voltammetry to monitor the deposition process, and it is possible to deposit a single (mono) layer. The process can only occur if the work function of the substrate is higher than that of the chosen metal. Since the work function of lead, 35.2 kJ mol^{-1} [2], is less than that of carbon, 122.5 kJ mol^{-1}, UPD is possible.

In order to evaluate this process samples were subjected to surface analysis using both X-ray photoelectron spectroscopy (XPS) and Secondary Ion Mass Spectroscopy (SIMS). XPS can be used to identify elements present in a sample directly from the kinetic energies of their photoelectrons which are ejected when the surface is bombarded by monoenergetic soft X-rays. For a solid, XPS is capable of probing 2–20 atomic layers deep, depending on the material, the energy of the photoelectron concerned and the angle (with respect to the surface) of the measurement [3]. For the latter reason flat specimens are recommended, and the analysis suggests problems can occur when using a fibrous substrate.

During SIMS analysis, element identification is obtained by monitoring the mass/charge ratio of secondary ions, which are produced when the sample surface is bombarded by an ionised beam. Ion-induced sputtering occurs when the kinetic energy transferred by the primary ions exceeds the bonding energy of certain atoms, and when the transmitted momentum has a component perpendicular to the surface [4]. Hence the fibrous nature of the samples could influence the level of lead that this method of analysis is able to identify.

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Positive ion emission was used as this favours an increase in the yield of positive ions (i.e., Pb^{2+} and Pb^{4+}).

2. Experimental methods

2.1. Production of lead coated carbon fibres

Lead coated polyacrylnitryl based high conductivity carbon fibres were produced using the UPD process, which is studied using cyclic voltammetry. Cyclic voltammetry involves measuring the current flowing through an electrode surface when a triangular waveform is applied at a constant sweep rate. The current is then plotted against the applied potential. The cell used when making these measurements consists of three electrodes partially immersed in the electrolyte. Platinum wire is used as the counter electrode with a mercury sulphate reference electrode. The working electrode is the deposition substrate which, in this instance, consisted of carbon fibre tows. The cell was linked to a Solartron–Schlumberger 1186 three-electrode potentiostat which was also connected to a potential waveform generator and X/Y chart recorder as shown in Fig. 1. The chart recorder provided a direct record of the current/voltage output which is commonly referred to as a 'cyclic voltammogram.' Peaks in the measured current can be attributed to reactions occurring at characteristic potentials. The peak width and height for a particular process may depend on the sweep rate, electrolyte concentration and the electrode material.

Initial calibration of the equipment was required prior to use. This was achieved by applying a load of 1000 ohms in place of the experimental cell to calibrate the voltage range. Output voltage was then checked using a multi-meter. A record of the output voltage was used to calibrate the current output, using Ohm's law and the nominal resistance.

For successful deposition the cell and electrodes must be free from organic and inorganic contaminants. Consequently, the cell was rinsed once in sulphuric acid and several times in double-distilled, de-ionised water. During the course of the experiment, the cell was stored *in situ* but maintained completely saturated with de-ionised water when not in use. After initial cleaning, the platinum wire electrode was heated in a Bunsen burner flame in order to remove contaminants by oxidation and evaporation. The reference electrode was rinsed carefully and stored in distilled water when not required. A fresh sample of carbon fibres was used for each voltammogram.

The four electrolytes tested are shown in Table I.

The equipment was assembled as shown in Fig. 1. Argon gas was bubbled through the electrolyte for a period of 20 minutes to remove oxygen before being introduced at the top of the cell to maintain an inert atmosphere. The electrodes were then inserted and connected to the potentiomer. The potentiometer provided a controlled variable potential across the cell during recording of the output. For deposition to occur the sample was cycled up to ten times, until bulk deposition was visible. When the sample was removed from the cell, the bulk layers and residual electrolyte were rinsed using de-ionised water. The samples were then air dried and stored in airtight containers prior to analysis.

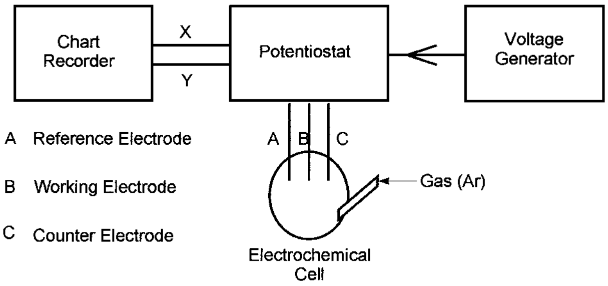

Figure 1 Layout of UPD equipment.

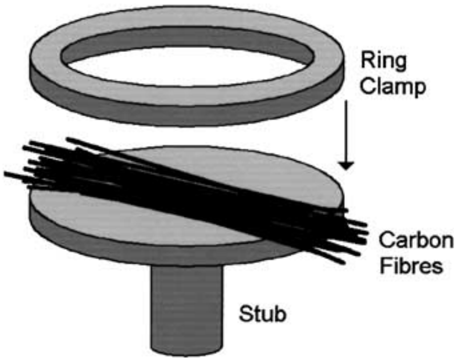

Figure 2 Mounted XPS specimen.

2.2. Surface analysis of lead coated carbon fibres

XPS and SIMS samples were mounted on pure copper stubs and clamped into position using a copper ring as shown in Fig. 2. A section of lead sheet was used as a standard for both methods of analysis.

2.2.1. Equipment and procedure

Both XPS and SIMS analysis methods required the sample chamber to be evacuated to a pressure of approximately 1.333×10^{-8} Nm^{-2} (1×10^{-10} torr). A more comprehensive description of the settings used for each technique is given below.

2.2.1.1. XPS settings. For XPS the X-ray source used was magnesium K_α radiation. The 50 eV analyser was capable of a maximum count rate of 194101 counts s^{-1} when using a step size of 0.60 eV and a dwell time of

TABLE I Electrolytes tested

(A)	Ammonium acetate (0.05 M)	Lead acetate (0.01 M)	Sodium sulphate (0.005 M)
(B)	Perchloric acid (0.1 M)	Lead acetate (0.01 M)	
(C)	Sulphuric acid (7.2 M)	Lead acetate (0.01 M)	
(D)	Nitric acid (1 M)	Lead acetate (0.01 M)	

TABLE II Summary of UPD conditions

Sample no.	Electrolyte	Voltage range (V)	No. of cycles	Additional information
1	A	0.65–(−0.01)	2	Pb deposited, started at 0.0 V
2	A	0.72–(−0.22)	4	Held at $V_{\max}$ for 2–3 mins
3	A	0.65–(−0.01)	1	Held at $V_{\max}$ for 2–3 mins
4	A	0.65–(−0.01)	1.5	—
5	A	0.65–(−0.01)	1	Blackening of Pt electrode noted
6	A	0.65–(−0.01)	1	C.F. mat impregnated with resin used as working electrode
7	A	0.65–(−0.01)	6	—
8	A	0.65–(−0.01)	2	Reduced quantity of carbon fibres in working electrode
9	B	0.65–(−0.01)	2	—
10	B	0.39–(−0.01)	7	—
11	B	0.39–(−0.01)	2	—
12	B	0.0393–(−0.017)	10	—
13	B	0.0393–(−0.017)	10	—
14	B	0.0393–(−0.017)	10	—
15	B	0.0393–(−0.017)	10	—
16	B	0.0395–(−0.017)	5	Held at 0.390 V at start
17	B	0.495–(+0.083)	4	Changed polarisation levels to achieve voltage range
18	B	0.562–(+0.15)	4	—
19	B	0.595–(+0.2)	2	—
20	B	0.35–(+0.2)	4	—

500 ms. The results were recorded and processed using a microcomputer. Results were plotted using the cumulative counts for each binding energy recorded. Once the scan was complete, individual peaks were examined and compared to corresponding binding energy ranges taken from a pure lead standard.

2.2.1.2. SIMS settings. Static surface analysis using SIMS was carried out using a positively charged argon primary ion source with an ion current density of 530 nA/mm^2 at 4.5 keV. The mass spectrometer was capable of a maximum count rate of 5610 counts s^{-1}, using a step size of 0.50 a.m.u. and a dwell time of 200 ms. As for XPS, the results were collated and processed using a microcomputer. The counts per channel were listed and the peak readings noted for comparison with those obtained for the lead standard.

3. Results

Four electrolytes, A, B, C and D, were used to produce bulk deposition. However, satisfactory voltammograms were only obtained using electrolyte A, lead acetate with ammonium acetate and sodium sulphate, or electrolyte B, lead acetate with perchloric acid. Multiple sweeps were employed to ensure that the maximum fibre surface area was coated with at least one layer of lead. During the course of this work 20 samples were produced. A summary of the UPD conditions for each sample is given in Table II. Lead was deposited on samples 1 to 8 using electrolyte A, and samples 9 to 20 using electrolyte B.

3.1. Observations of the deposition process

It was observed that the perchloric acid based electrolyte produced a uniform bulk deposition, covering all carbon surfaces, whereas the ammonium acetate electrolyte tended to favour bulk deposition at the ends of the carbon fibres, i.e., on the fracture surfaces, perpendicular to the fibre length. Fig. 3 shows a voltammogram obtained for pure lead. Reduction of Pb^{4+} to Pb^{2+} occurs at a potential of approximately 0.45 V. Reduction of Pb^{2+} to Pb^0 occurs gradually over a potential range of +0.37 to −0.4 V.

TABLE III Summary of surface analysis results

Sample no.	Analysis method	Pb identified?
8	SIMS	×
16	XPS	√
Pb (1)	SIMS	√
Pb (2)	XPS	√

Examination of the voltammogram produced for sample number 16 revealed that the observed deposition lies in the range for bulk deposition, occuring at a potential of approximately 0.262 V. The dip associated with the underpotential deposition is very shallow, indicating the low quantity of lead deposited. The peak does not occur in the second or third cycles. Bulk deposition begins at a potential of approximately 0.116 V, resulting in an underpotential shift of ∼146 mV. An equivalent peak was not observed for sample 8.

3.2. Surface analysis

The best multi-layer coverage was achieved with the perchloric acid based electrolyte. However a sample was taken from each electrolyte group for surface analysis. Sample 8 was examined for the presence of Pb ions using SIMS and sample 16 using XPS. A standard sample of Pb was also analysed using each method. A summary of the surface analysis results is given in Table III. Peaks corresponding to Pb were observed in the standard lead sample analysed using SIMS. However, the values obtained for atomic masses of the isotopes were 0.2 a.m.u. higher than characteristic values. The standard sample examined using XPS also deviated for recognised values for lead by approximately 2 eV. This phase shift could be a result of one or more factors

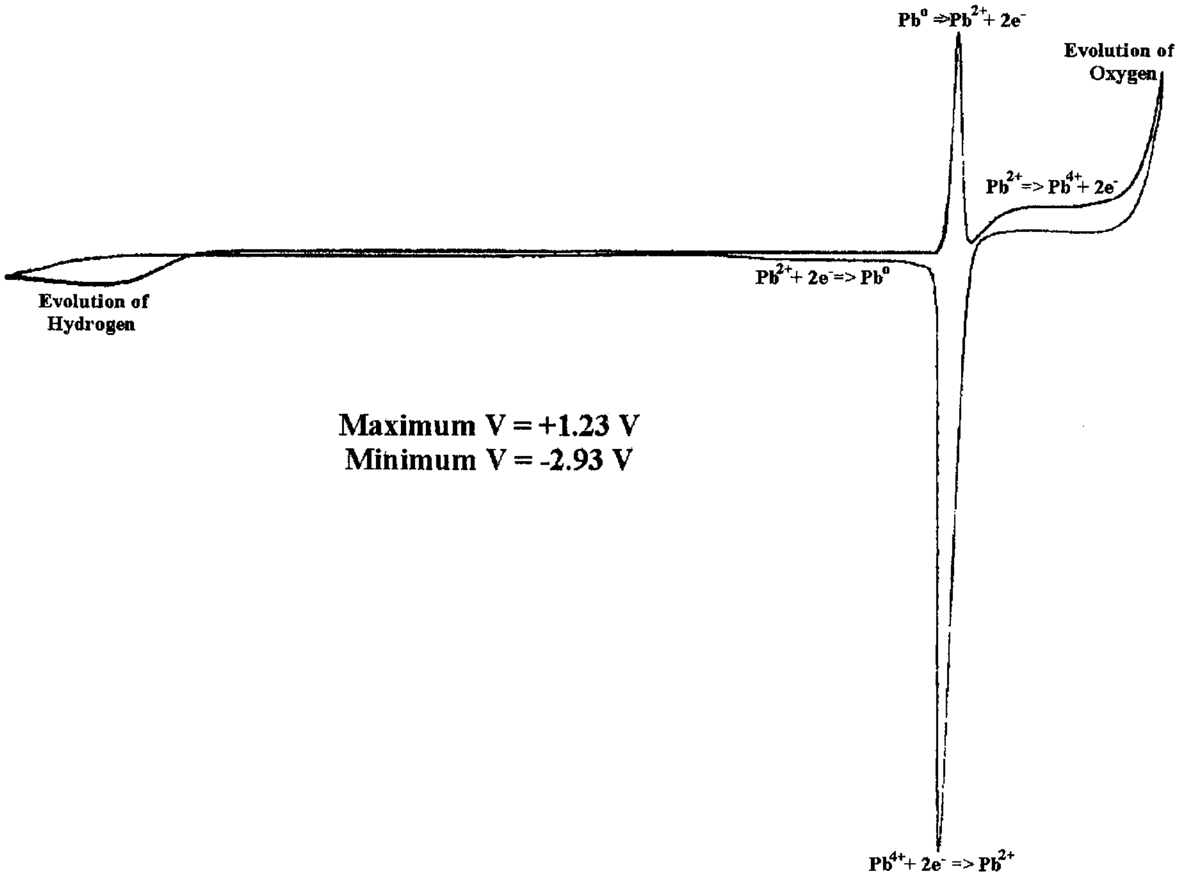

Figure 3

such as charging of the surface oxide layer or bonding of the Pb ions to oxygen, since the values will depend on both the crystal and defect structures of PbO. With the current results it is not possible to be more specific than this.

4. Conclusions

The following conclusions have been drawn from the results.

- The electrolyte composed of 0.1 M $HClO_4$ and 0.01 M $Pb(OAC)_2$ produced a detectable lead coating.
- Underpotential deposition of lead onto carbon fibres in this electrolyte occurs at a potential of ∼262 mV, with an underpotential shift of 0.146 mV.

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