

# Voltammetric Determination of Trace Amounts of Copper, Cadmium and Lead in Lead - Acid Battery Electrolyte

Pier Luigi Buldini, Praveen Saxena,\* Vibha Saxena† and Alessandro Toponi

CNR - Lamel, Laboratorio Analisi Chimica dei Materiali, Via dell'Idraulico 17/2, I 40138 Bologna, Italy

Voltammetric techniques were used for the simultaneous determination of copper, cadmium and soluble lead in lead - acid battery electrolyte without any manipulation of the sample, thus allowing the sample to be returned to the battery if required. The proposed method consists in transferring 10 ml of 38%  $\text{H}_2\text{SO}_4$  directly into the voltammetric cell and, after de-aeration, the solution was subjected to differential-pulse anodic stripping voltammetry for the determination of cadmium and soluble lead and to differential-pulse polarography for the determination of copper. The responses were at  $-0.600$ ,  $-0.435$  and  $-0.005$  V *versus* an Ag - AgCl reference electrode for cadmium, lead and copper, respectively. The responses were proportional to the respective metal concentrations from at least  $0.03$  to more than  $1-5 \mu\text{g ml}^{-1}$  in 38%  $\text{H}_2\text{SO}_4$ , with a relative standard deviation of 2-3% at  $0.06 \mu\text{g ml}^{-1}$ . The results were checked by cold vapour atomic absorption spectrometry. The effect of other ions on the proposed method was also evaluated.

**Keywords:** Copper, lead and cadmium determination; voltammetry; sulphuric acid; battery

The lead - acid battery still represents the most important electrochemical system for energy storage in spite of its age and is expected to maintain this role at least in the near future; for this reason it is still the subject of extensive research.

In this context, the present work was undertaken as part of a wider study to investigate the dissolution, transport and sorption of trace elements in the lead - acid cell during its cycling (*i.e.*, during the number of charge/discharge cycles that represent the life of the battery). The performance of the cell depends on its various constituents, *viz.*, positive and negative active material, grids, electrolyte, separator, etc. The influence of current density, temperature, characteristics of the electrodes and other factors that can lead to exhaustion of the active material have been widely studied. The complexity of sulphuric acid as the electrolyte in the porous lead dioxide electrode is due not only to its two dissociation steps and the low solubility of lead sulphate, but also to the fact that sulphate ions are specifically adsorbed on the lead dioxide surface. However, little information is available about the state of the electrolyte and the influence of the various elements that pass into solution during the electrochemical cycle.

The present work is concerned with the influence of some of the impurities that dissolve in the electrolyte during the charge/discharge cycles and their effect on the decline in performance and eventual failure of the battery. The transport of metal impurities is a critical factor limiting cell performance: over a period of time, metals contaminate the active material and hence lower the hydrogen overvoltage, directly influencing the charging efficiency.

For instance, the deposition of copper on the negative grid by some manufacturers for improving the electrical conductivity may have an adverse effect during the life of the battery because, after a sufficient number of cycles, the copper completely dissolves in the electrolyte taking part in conduction and reduces the content of ionic lead involved in the electrochemical process.

The present work deals with the investigation of some of the chemical species in the lead - acid battery electrolyte during the course of cycling. The information obtained could be useful for the solution of both technical and manufacturing

problems and may provide a deeper insight into the processes determining the performance of the lead - acid battery.

Flame and cold vapour atomic absorption spectrometry (AAS)<sup>1-3</sup> and also voltammetric techniques<sup>4-7</sup> have been applied to the determination of trace amounts of copper, lead and cadmium in sulphuric acid. The sensitivity of both these techniques is adequate. However, whereas AAS techniques require solvent extraction of metal chelates or evaporation of the sample to dryness and do not permit simultaneous determinations, voltammetric techniques can determine copper, cadmium and soluble lead simultaneously, and only require removal of the oxygen and sulphur dioxide dissolved in the sample using a stream of pure nitrogen.

The aim of this work was to develop a simple, rapid and reliable method for routine use, without the need for sample manipulation, in order to automate the collection of data from on-line battery banks during cycling and correlate the data with the electrical phenomena observed; for this purpose computer-controlled equipment was employed.

The proposed method consists in directly analysing 10 ml of 38% sulphuric acid, after de-aeration, by applying differential-pulse anodic stripping voltammetry (DPASV) for the determination of cadmium and lead and then determining copper by differential-pulse polarography (DPP). Differential-pulse anodic stripping voltammetry could not be used to determine copper because of the lack of reproducibility.

## Experimental

### Reagents

Erbatron electronic grade sulphuric acid was used and normal precautions for trace analysis were taken throughout.

Ultrapure water with a resistivity of  $18 \text{ M}\Omega$  was obtained from a Millipore Milli-Q water purification system.

Prior to use, all glassware was washed with concentrated sulphuric acid, allowed to stand overnight, then rinsed in ultrapure water.

Working standards were prepared by diluting Normex (Carlo Erba) atomic absorption standards ( $1000 \mu\text{g ml}^{-1}$ ) as necessary.

### Apparatus

The instrument used for the voltammetric measurements was a Metrohm (Herisau, Switzerland) 646 VA processor equipped with a 647 VA stand, a 675 VA sample changer and 665 VA Dosimat automatic addition burettes. The working

\* Permanent address: Department of Non-conventional Energy Sources, Block 14, C.Cr.O. Complex, Lodi Road, 110 003 New Delhi, India.

† Permanent address: J.R.F., Department of Chemistry, University of Delhi, 110 007 Delhi, India.

electrode was a multi-mode electrode (MME), the reference electrode was Ag - AgCl ([KCl] = 3 M) and a platinum tip *ca.* 65 × 2 mm was used as the auxiliary electrode.

The operating conditions of the 646 VA processor are given in Table 1. The analysis time (including the de-aeration step and two replicate determinations of each element) was 17 min.

A 10-ml cell was normally used. Solutions were de-aerated with pre-saturated pure nitrogen for 2 min before analysis and thermostated at 25.0 ± 0.1 °C.

For confirmation purposes, AAS measurements were made with a Varian AA-875 ABQ instrument equipped with a GTA-95 graphite tube atomiser. The furnace was purged with 99.9% pure argon.

Study of the Polarographic Working Conditions

The polarographic behaviour of copper, lead and cadmium is well known.<sup>8</sup> Because 4.4–5 M sulphuric acid is used as the lead - acid battery electrolyte, attempts were made to utilise the same acid concentration as the supporting electrolyte.

Yasumori and co-workers<sup>4-6</sup> described the polarographic behaviour of lead and copper in sulphuric acid. They found that the peak potential of lead was shifted towards negative values with increasing sulphuric acid concentrations and overlapped the hydrogen discharge when the concentration exceeded 12 M. On the other hand, the peak potential of

copper was found to overlap the mercury anodic oxidation curve when the sulphuric acid concentration was greater than 6 M.

In our experiments, it was found that the optimum supporting electrolyte concentration range for obtaining well defined peaks, permitting the simultaneous determination of copper and lead, was 4.5–5 M sulphuric acid. This range is close to that of the sulphuric acid normally used as the lead - acid battery electrolyte; hence its direct analysis is possible without any sample manipulation.

When the instrumental parameters given in Table 1 are used, the peak potential of Pb<sup>II</sup> is sufficiently far from that of Cd<sup>II</sup> (more than 0.15 V) to permit the determination of as little as 30 ng ml<sup>-1</sup> of cadmium in the presence of a 25 : 1 excess of lead, with a relative standard deviation of 8% at the detection limit. A detection limit of 30 ng ml<sup>-1</sup> was also obtained for copper, mainly due to the closeness of the copper peak to the mercury anodic oxidation curve. In addition, lead can be detected down to 10 ng ml<sup>-1</sup> or less, with a relative standard deviation of 4%. For all three elements a linear calibration graph was obtained from the detection limit to 1–5 µg ml<sup>-1</sup>.

In this work the two most sensitive electroanalytical techniques, *i.e.*, DPASV and DPP, have been compared and the former was found to be the more suitable for the determination of lead and cadmium, whereas the latter gave the best results for copper. With DPASV the intermetallic compounds that are deposited during the pre-electrolysis step prevented a signal reproducibility of better than 15–25% being achieved for copper.

When using DPASV for the determination of lead and cadmium, the pre-electrolysis potential was maintained at –0.750 V for cadmium, and then at –0.550 V for lead, for a period of 80 s; the stirring (at 2270 rev min<sup>-1</sup>) was stopped 20 s before the pre-electrolysis was complete and the cell voltage was then scanned at 10 mV s<sup>-1</sup>. After the determination of cadmium and lead the parameters were changed automatically so that DPP could be used to determine copper, thus completing the analysis of the sample in a single run.

Effect of Foreign Species

More than 30 elements, including Ag, Al, As<sup>III</sup>, As<sup>V</sup>, B, Ba, Bi, Ca, Ce, Co, Cr<sup>III</sup>, Cr<sup>VI</sup>, Fe, Ge, In, Mg, Mn, Mo, Ni, P, Pt, the rare earths, Ru, Sb<sup>III</sup>, Sb<sup>V</sup>, Si, Sr, Ti, V, W<sup>VI</sup>, Zn and Zr were tested. It was found that Ag and Mo interfered with the determination of copper even when present at concentrations lower than that of copper. Arsenic(III) must be completely absent when determining both cadmium and lead. Antimony and V interfered with the cadmium peak even when their concentrations were only one tenth of that of cadmium.

No interference was observed in the presence of more than a 200-fold excess of the other elements studied.

Procedure

A 10-ml volume of the battery electrolyte was taken and de-aerated for 2 min. The programme summarised in Table 1 was used to determine cadmium by DPASV after pre-elec-

Table 1. Polarographic conditions

Drop size . . . . .	<i>ca.</i> 0.55 mm <sup>2</sup>
Electrode type* . . . . .	MME operated as DME for Cu and as HMDE for Cd and Pb
Measuring mode . . . . .	DPP for Cu; DPASV for Cd and Pb
Pulse amplitude . . . . .	50 mV
Drop time (for Cu only) . . . . .	600 ms
Pre-electrolysis time (for Pb and Cd) . . . . .	80 s
Stirring speed . . . . .	2270 rev min <sup>-1</sup>
Quiescent period before the end of pre-electrolysis . . . . .	20 s
Pre-electrolysis potential . . . . .	–0.750 V for Cd and –0.550 V for Pb, <i>versus</i> Ag - AgCl
Potential sweep . . . . .	–0.750 to –0.475 V (Cd); –0.550 to –0.310 V (Pb); +0.100 to –0.150 V (Cu)
Scan rate . . . . .	10 mV s <sup>-1</sup>
Voltage step . . . . .	6 mV
Time step for measurement . . . . .	600 ms
Peak width range (min.–max.) . . . . .	21–246 mV
Tolerance on verification voltage . . . . .	±35 mV
Peak asymmetry (max.) . . . . .	9%
Purge time . . . . .	120 s
No. of replications . . . . .	3 (average value calculated over 3 replications)
Standard additions . . . . .	50 µl of 10 µg ml <sup>-1</sup> standard solutions
No. of standard additions . . . . .	3
Vessel volume . . . . .	10 ml

\* MME = Multi-mode electrode; DME = dropping mercury electrode; and HMDE = hanging mercury drop electrode.

Table 2. Determination of cadmium, soluble lead and copper in lead - acid battery electrolyte (38% H<sub>2</sub>SO<sub>4</sub>)

No. of cycles	Cu/µg ml <sup>-1</sup>		Cd/µg ml <sup>-1</sup>		Pb/µg ml <sup>-1</sup>	
	Cold vapour		Cold vapour		Cold vapour	
	DPP	AAS	DPASV	AAS	DPASV	AAS
0	0	0	0	0	0	0
10	0.03	0.04	0.02	0.02	1.62	1.70
100	0.55	0.51	0.40	0.43	2.05	2.00
500	1.20	1.24	1.32	1.27	4.35	4.13
1000	2.75	2.74	3.15	3.23	2.88	2.97
1500	7.50	7.25	4.04	4.16	2.76	2.75

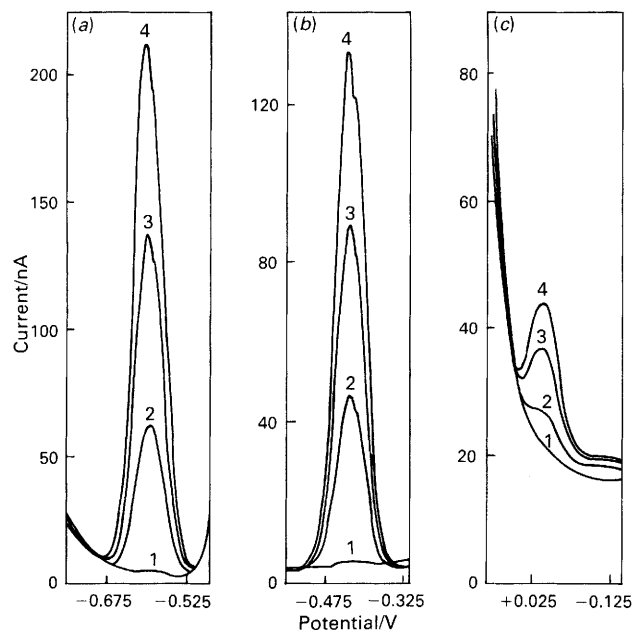


Fig. 1. (a) Cadmium, (b) lead and (c) copper peaks in 38%  $\text{H}_2\text{SO}_4$ . 1. Blank, i.e., battery electrolyte before start of cycles; 2, battery electrolyte after ten cycles; and 3 and 4, successive additions of 50  $\mu\text{l}$  of standard cadmium(II), lead(II) and copper(II) solutions ( $10 \mu\text{g ml}^{-1}$ ) to 10 ml of the sample electrolyte (2)

trollysis at  $-0.750 \text{ V}$  versus Ag - AgCl for 80 s, then lead after a similar pre-electrolysis step at  $-0.550 \text{ V}$  versus Ag - AgCl. After the data relating to sample and standard additions had been collected, the measuring technique was changed to DPP and the polarograms of copper were recorded from  $+0.100$  to  $-0.150 \text{ V}$ . The procedure was repeated twice more in order to obtain an average value with a reduced relative error.

### Results

In order to test the proposed method, lead - acid batteries were examined under different cycling conditions. Typical results are presented in Table 2.

The results obtained by voltammetric measurements were compared with those obtained by cold vapour AAS, following the procedure described by Langmyhr and Haekedal,<sup>2</sup> and these results are also given in Table 2.

Fig. 1 shows a typical series of voltammograms obtained on a real sample. In the voltammogram of copper the tail-end of

the mercury anodic oxidation curve is visible; its closeness effectively limits the detection of copper.

The standard deviation of the spectrometric data was generally higher than that of the voltammetric data, probably due to the sample manipulation required in the cold vapour atomic absorption procedure (evaporation to dryness in vitreous-carbon boats).

It is interesting to note that the cadmium and copper contents in the electrolyte increase as the battery ages.

It is not fully understood why the lead content fluctuates in an apparently random fashion during battery cycling; it appears that it is not simply a result of the thermodynamically controlled lead sulphate precipitation process.

Experiments are currently being carried out in this laboratory on the same type of lead - acid battery at different temperatures, in a controlled environment, from the beginning of the cycle to cell failure, in order to establish a relationship between the age of the battery and the impurities present.

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