Volume 1986 | Number 4

10-7-1986

Surveying Battery Cell Sections to Determine the Composition and Spatial Distribution of Discharge Products using an Automated Microprobe

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Surveying Battery Cell Sections to Determine the Composition and Spatial Distribution of Discharge Products using an Automated Microprobe

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Abstract

Determining the spatial distribution and composition of hydrohetaerolite in polished sections of discharged Leclanché cells requires the measurement of oxygen concentrations on microcrystalline material. This can be done if the composition of the mounting medium is included in the matrix correction of raw intensities. The method of Pouchou and Pichoir (PAP) is used initially to correct raw intensities obtained from surveys of microcrystalline standard material. Mean analyses agree well with the known compositions provided a correction is made for the oxygen content of the mounting medium. The same correction is then applied to the raw data collected when surveying cell sections, yielding spatially correlated analyses of hydrohetaerolite formed as a discharge product. The surveying technique could be applied to lead-acid, Leclanché and alkaline cells.

Introduction

The formation of hydrohetaerolite type materials \( \text{Mn}_2\text{O}_3 \cdot \text{MnO}^{(1-x)} \cdot \text{ZnO}^{(x)} \cdot y\text{H}_2\text{O} \) as a discharge product in Leclanché cells made using Groote Eylandt manganese dioxide has been proposed by Swinkels and Ward [12]. They present the results of automated microprobe surveys of cell sections which show the variation of the parameters \( x \) and \( y \) with position in the cell and with depth of discharge of the cell. The purpose of the present paper is to describe this surveying technique and the novel way in which matrix corrections were applied to determine \( x \) and \( y \) for aggregates of submicron-sized particles. A micrograph of a cell section showing this microcrystalline material is shown in Fig. 1.

\[
x = \frac{3\text{Zn}^+/\text{(Mn}^+ + \text{Zn}^+)} {y = \frac{30^+/\text{(Mn}^+ + \text{Zn}^+)}{4} - 4}
\]

Key Words: Electron microprobe, microanalysis, microcrystalline, battery, Leclanché, Manganese dioxide, hydrohetaerolite, light element, X-rays.

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The parameter \( x \) is found from:

\[
x = \frac{3\text{Zn}^+/\text{(Mn}^+ + \text{Zn}^+)}
\]

and \( y \) from

\[
y = \frac{30^+/\text{(Mn}^+ + \text{Zn}^+)}{4} - 4
\]
where Mn', Zn' and O' refer to atom fractions.
Microcrystalline material presents irregular target surfaces with respect to the electron beam. However, the ratio of the manganese and zinc X-ray intensities is only marginally affected by the tilt of a target surface because their Ka X-rays are of similar energy. So, x can be determined with fair accuracy for porous or microcrystalline targets. The accuracy with which the hydration parameter y can be determined depends on how accurately oxygen can be determined. Light-element analysis has been considered to be difficult for well polished specimens because the matrix corrections are very large. It is even more difficult for cell sections in which the target is very often microcrystalline or porous.

A number of approaches have been taken in dealing with microcrystalline material. Russ and Hare [10] derived raw intensity data from energy dispersive spectrometry (EDS) for a large number of points and identified clusters in multidimensional element space. As a first approximation correction for porosity, raw intensities were normalized to backscattered electron intensity. The centroids of clusters were then treated by the classical methods of correction or associated with phases expected on other grounds to be present in the material. Statham [11] used the fact that the ratio of peak-to-background is largely independent of surface tilt so that this ratio is relatively insensitive to surface roughness. However, the long counting times required to measure background would be impractical in a cell survey since several thousand analyses must be accumulated to obtain statistically significant data on the spatial distribution of species.

The present approach follows that of Russ and Hare [10] in that raw intensities or k-ratios for Mn, Zn and O are collected for several thousand points so that their distributions can be studied. To correct this raw data for matrix effects, it is assumed that all targets can be described as a homogeneous mix of the oxide, oxygen and carbon, the last two being contributed by the mounting medium. This is called the "epoxy mix model". Recently available software by Pouchou and Pichoir (PAP) [8] is used to compute corrected concentrations for manganese, zinc and oxygen with carbon included in the calculations by difference.

### Specimen Preparation

#### Standards

Anhydrous hetaerolite type-materials, with compositions ranging from haussmanite (x = 0, y = 0) to hetaerolite (x = 1, y = 0), were prepared at BHP Central Research Laboratories (CRL) by heating mixtures of ZnO and electrolytic manganese dioxide (EMD) to 900°C in air overnight [12]. After annealing they were found to be homogeneous in composition when analyzed in a Philips 505 SEM/EDAX system, although they varied widely in texture. Those samples with less than about 20% by weight of zinc had numerous uniform grains 30 µm or more in diameter suitable for use as probe standards. Stoichiometric MnO, (standard A) was used as a standard for manganese and oxygen and the standard used to determine zinc was a hetaerolite sample containing 19.9 wt.% zinc (standard B). A further standard sample containing 27.3 wt.% zinc (standard C) was found to be very fine-grained and of all standards prepared was closest in texture to battery section material. Along with standard B, it was used to test the validity of the matrix correction procedure. Micrographs of standards B and C are shown in Figs. 2 and 3 respectively. Table 1 contains weight fractions and relevant X-ray count rates for all three standards. Although they are anhydrous, the standard materials are close in composition to that expected for the discharge products, so matrix correction errors are small and peak shift for 0 Ka between standards and unknown is negligible.

### Table 1. Chemical data and count rates for standards A, B and C (y = 0).

<table>
<thead>
<tr>
<th>Std</th>
<th>x</th>
<th>Mn</th>
<th>Zn</th>
<th>O</th>
<th>MnKa</th>
<th>ZnKa</th>
<th>OKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.</td>
<td>0</td>
<td>0.720</td>
<td>0.000</td>
<td>0.280</td>
<td>8500</td>
<td>-</td>
<td>2200</td>
</tr>
<tr>
<td>B.</td>
<td>0.72</td>
<td>0.530</td>
<td>0.199</td>
<td>0.271</td>
<td>-</td>
<td>1520</td>
<td>-</td>
</tr>
<tr>
<td>C.</td>
<td>1.00</td>
<td>0.457</td>
<td>0.273</td>
<td>0.270</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Standard samples were mounted in epoxy resin in holes drilled in a 25 mm brass block along with a standard of highly pure pyrolusite (δ-MnO₂) which was used to check for drift in the oxygen Ka count rates during surveys. The mounting epoxy (Epirez Epsilon) was doped with 20 wt.% of finely powdered graphite. The face of the block was then ground flat to expose the grains of manganese/zinc oxide, polished on diamond laps and finally lapped on 0.5 µm Al₂O₃ powder using water as a lubricant to minimize temperature rise. The block was then coated with 10 nm of aluminum.

#### Battery Sections

Swinkels and Ward [12] described in detail how battery material was manufactured and how sections were made by cutting 10 mm thick discs from the cell that had been frozen in liquid N₂. After washing with NH₄Cl, to minimize precipitation of basic ZnCl₂, each disc was dried, set in epoxy, doped with graphite and backfilled under vacuum with Loctite. Light lapping on 1 µm diamond for 6 min before coating exposed the maximum amount of battery material without loosening the surface. Diamond lapping was chosen in preference to Al₂O₃ to avoid embedding extra aluminum-rich material into the section.

#### Aluminum coating

The polished cell sections were coated with 10 nm of aluminum before surveying. At the beam conditions chosen for the microprobe work (15 kV, 50 nA, spot diameter 2 µm includes 99% of excitation [9]), it was found that 25 nm of carbon or
Microprobe Surveying of Leclanche Cell Sections

10 nm of aluminum was required to give a stable film. Although the stopping power of the two films is similar, the absorption of 0 Ka X-rays is less for aluminum. According to Henke and Ebisu [3], the mass absorption coefficients for 0 Ka in Al and C are 6,715 and 12,380 cm²/g respectively. For the given film thicknesses and a 40° take-off angle, the losses in intensity for 0 Ka X-rays in Al and C are 2.8% and 6.1% respectively. Therefore, errors in coating thickness measurement or non-uniformity of coat are less critical for aluminum.

Another reason for choosing aluminum is that its thermal conductivity is higher than that of carbon, giving a significant reduction in temperature rise at the specimen surface. By applying a formula derived by Friskney and Haworth [2], the temperature rise in a manganese oxide grain 50 µm in diameter for a beam spot size of 1 µm would be less than 150°C with aluminum coating. The formula cannot be applied directly for smaller grains or for porous material but it is considered that this worst-case calculation would set an upper limit because the target is always embedded in a conducting medium. McAndrew [5] has shown that there is some loss of water from hydroheterolite on heating below 400°C. Repeated counts of 1 s duration on aluminum-coated synthetic hydroheterolite using the beam conditions of the surveys (50 nA at 15 kV) showed no significant change in manganese, zinc or oxygen count rates for the first 8 s of beam residence. After a further 30 s residence a drop in the oxygen count rate of 5% occurred with a similar rise in both the Mn and Zn rates. Since the peak counts are recorded within 3 s, the errors introduced by heating are negligible.

The surface of the Al coating oxidizes rapidly in air and partial oxidation occurs during the coating process, particularly if this is slow. The metal was deposited at a minimum rate of 0.8 nm/s at pressures lower than 10−5 mm of Hg. Using the method given by Maurice et al. [4] and a highly oxidized coat as a standard, it was found that the oxygen weight fraction in the coating was always less than 26 wt.%. Since aluminum reports at less than 1% on the standards, the error introduced in the measurement of oxygen is less than 0.26 wt.%. This is not significant since it is common to both standard and unknown.

Survey Strategy

Survey Hardware + Software

The cell section surveying was carried out on a Cameca "Camebax" microprobe fitted with a LINK SYSTEMS energy dispersive spectrometer (EDS) and three wavelength-dispersive spectrometers (WDS), all having a take-off angle of 40°. Software written in Fortran 4P for the DEC PDP 11/23 computer calls subroutines supplied by Cameca in the "MICBEA" library to achieve control of the stage, beam and spectrometers. The stage was moved so that the stationary beam was targeted on points lying on four radii covering a quadrant of a cell section. At each point, information collected included the current normalized X-ray count rates, absorbed current, backscattered electron current and the stage coordinates.

Setting up the parameters of a survey

Parameters of the survey which could be selected were step size, total line length, counting time for WDS and EDS systems, beam current, beam accelerating voltage, standards used to derive k-ratios, elements and X-ray lines, pulse height analyser mode, background correction mode, on-line discriminator levels and two linear imaging parameters which are described below.
Background measurement

For trace elements, backgrounds were measured at spectrometer positions either side of the peak. For major elements, the backgrounds were estimated by going to a position above the peak and calculating the under peak value using the gradient of the background curve. This gradient is available from firmware supplied by Cameca. Oxygen background can only be measured in this way since low background positions are too close to a Mn L1 line. Moving the spectrometers is slow so that, for example, if total counting time on peak and background is 1.5 s, the total time using a single background measurement is 5.5 s. This is the major factor limiting the speed of the surveys.

Oxygen sensitivity check

The pulse height analyser on the light elements spectrometer was tuned by selecting preamplifier chips and by setting the gas gain with the help of a monitor multichannel analyser (TN1705). However, small changes in atmospheric pressure can change gas gain and hence the count rate. As well, a reduction in oxygen count rate with time was observed (about 8% in 1 h and then stabilizing), the cause of which has not yet been determined. To compensate for drift of both types, the stage was driven back to a highly pure and homogeneous pyrolusite standard every 20 min and 50,000 counts were collected. This was converted to a normalized count rate and compared to that measured at the beginning of the survey. A correction was then made to subsequent oxygen count rates. At each sensitivity check, a fresh point was taken on the pyrolusite standard to avoid the effects of contamination.

Correction for Specimen plane tilt

With our polishing techniques, the surfaces of our 25 µm samples are "flat". Relief caused by different hardness material is not alone sufficient to defocus the WD spectrometers. However, even though the Cameca microprobe is furnished with a top referencing stage, defocusing can still occur due to surface tilt. Three well separated and well focused points were loaded for each block surveyed and refocusing of the stage was performed after each 1000 µm traversed by interpolating between the stored coordinates.

On-line discrimination by absorbed current

The central carbon electrode and mounting plastic are of no electrochemical interest. Both materials have high absorbed current and are rejected for WDS measurement by establishing a discriminator level. If this value is exceeded, the stage is stepped to the next point. If it is not, the program proceeds to the EDS testing described below.

On-line discrimination by EDS

The EDS system is used to test points for unwanted elements such as aluminum, silicon and iron which occur in contaminant grains. Basic zinc chloride, a discharge product which was not removed completely by washing, was also identified using the Cl Ka peak from the EDS. Each spectrum is stored in the PDP 11/23 computer through SIRONCMA, a rapid successive approximation pulse height analyser designed and built by CSIRO which accepts pulses from the Harwell pulse processor of the LINK system. A point is rejected if there are less than 50 c/s of Mn Ka and also if the sum of counts for the four unwanted elements is greater than one-third of the manganese count. "Counts" here refers to the sum of the three channels around the previously measured peak position for that element. No background correction has been applied and the discriminator levels have been set empirically by examining a large number of random targets.

On-line particle definition

The definition of particles in battery sections using one-dimensional imaging techniques is often impossible. However, a particle definition routine was included in the software because many of the larger grains could be well defined. The minimum number of consecutive points, P1, passed by both discriminators can be selected. This defines the minimum particle size. It is also possible to choose the maximum number of non-accepted points within a particle, P2. Thus, a particle having a small internal void would still be defined correctly as one particle and not two.

Results and Discussion

Preliminary analyses for Mn, Zn, O and C

Twenty randomly selected points from a highly discharged battery were analysed for all four elements - Mn, Zn, O and C. The PAP corrected concentrations are presented in Table 2. Analyses are ranked in order of decreasing uncorrected total for the elements manganese, zinc and oxygen. With the exception of the eighth, these analyses could have been obtained from a truly mixed target since reasonable analytical totals are obtained. The eighth could be due to the beam straddling a boundary between plastic and a large solid grain, with the direction of the interface towards the light elements spectrometer port giving elevated k-ratios. Note that every analysis except one returned some fraction of carbon supporting the need to include it in the correction procedure since it has such a high absorption for 0 Ka X-rays. Analyses 14 to 20 would have to be rejected because the matrix correction factor for oxygen is too high (02.0) causing large errors in y. Such preliminary work suggested that if the amount of carbon in the mix was limited by selecting high raw totals (kMn + kZn + kO > 50%) and if a correction was applied for the oxygen content of the epoxy resin mounting medium, it might be possible to make first approximation analyses of battery material. Points such as the eighth would probably occur with low enough frequency that mean analyses would not be greatly affected.

Output of surveys

Each survey yielded around 3,000 valid data points out of a possible 12,000 after absorbed current and EDS discrimination. Typically, each battery section was surveyed in about 6 h. The step size was 5 µm, the EDS acquisition time was 0.5 s and the WDS counting time was 1.0 s. P1 and P2 were 1 and 0 respectively so that no data
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from small particles were rejected and no attempt was made to allow for internal voids.

Figures 4 and 5 are plots of measured k-ratios versus total for manganese, zinc and oxygen, collected by running a survey on standard C. The oxygen plot shows greater scatter even though oxygen count rates are higher than those of zinc. This is because the absorption of oxygen Kα X-rays is very large so that the measured intensities will be far more dependent on the topography of the target.

Fig. 4. Measured k-ratios for Mn and Zn from a survey of standard C plotted against the sum of k-ratios for all elements analysed (wt.%).

A plot of x versus raw total for standard C, given in Fig. 6, shows that zinc is reduced proportionally more than manganese as the totals fall below 70%. However, calculations using PAP show that for proportions of carbon up to 60 wt.%, the (Zn/Mn)-ratio should remain constant. This may be explained by noting that some grains are totally covered by epoxy. For such a target, the average beam energy at excitation is reduced. However, the "excitation error" for zinc would be reduced proportionally more than that for either manganese or oxygen. Only points having raw totals greater than 55% were used to compute x and y values for the radial dependence studies reported by Swinkels and Ward [12]. As noted above, rejection of low totals is necessary anyway since matrix corrections are too large for oxygen when carbon is high.

Table 2. Analysis of twenty randomly selected points on the polished section of battery Y1334. Mn, Zn, C and O were measured directly and corrected using PAP.

<table>
<thead>
<tr>
<th>Corrected wt.%</th>
<th>k-ratio Mn+Zn+O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>Zn</td>
</tr>
<tr>
<td>1</td>
<td>61.1</td>
</tr>
<tr>
<td>2</td>
<td>52.1</td>
</tr>
<tr>
<td>3</td>
<td>56.8</td>
</tr>
<tr>
<td>4</td>
<td>50.8</td>
</tr>
<tr>
<td>5</td>
<td>51.4</td>
</tr>
<tr>
<td>6</td>
<td>55.2</td>
</tr>
<tr>
<td>7</td>
<td>51.0</td>
</tr>
<tr>
<td>8</td>
<td>52.3</td>
</tr>
<tr>
<td>9</td>
<td>49.1</td>
</tr>
<tr>
<td>10</td>
<td>48.9</td>
</tr>
<tr>
<td>11</td>
<td>41.7</td>
</tr>
<tr>
<td>12</td>
<td>44.5</td>
</tr>
<tr>
<td>13</td>
<td>39.5</td>
</tr>
<tr>
<td>14</td>
<td>34.9</td>
</tr>
<tr>
<td>15</td>
<td>32.3</td>
</tr>
<tr>
<td>16</td>
<td>23.7</td>
</tr>
<tr>
<td>17</td>
<td>21.7</td>
</tr>
<tr>
<td>18</td>
<td>17.9</td>
</tr>
<tr>
<td>19</td>
<td>17.2</td>
</tr>
<tr>
<td>20</td>
<td>10.2</td>
</tr>
</tbody>
</table>

* = Element with PAP factor >2.0.

Fig. 5. Measured k-ratios for O from a survey of standard C plotted against the sum of k-ratios for all elements analysed (wt.%).

Fig. 6. Calculated x-values for hetaerolite from a survey of standard C plotted against the sum of k-ratios for all elements analysed (wt.%).
Correction of raw survey data

The matrix corrections were done in effect using PAP with carbon calculated by difference. However, the calculation time was reduced in the following way. Using the off-line version of PAP and assuming an epoxy mix model, k-ratios for hydrohetaerolite species having x values from 0.0 to 1.5, carbon weight fractions from 0.0 to 0.6 and y values from 0.0 to 3.0 have been computed. The hydrogen weight fraction has been added to the oxygen value. A regression analysis which takes the k-ratios for manganese, zinc and oxygen as independent variables was applied to relate the k-ratios to corrected concentrations. The correction formulae for each element are cubic in all three raw k-ratios with R-values greater than 0.99. These formulae are applied to the large number of raw k-ratios generated in a survey at the same time data is stored without adding significantly to survey time.

Some of the measured oxygen is not chemically bonded to the hydrohetaerolite but this does not invalidate the correction algorithm. If R₀ is the ratio of oxygen to carbon in the mounting medium, the wt.% assigned to hydrohetaerolite O" is given by:

\[ O" = O' - C' \cdot R₀ \]  

where the single primed values are those corrected by the rapid algorithm. However, R₀ cannot be estimated accurately. Both standards and battery sections have been prepared with graphite-doped epoxy resin but battery sections also contain about 7% acetylene black which is used in their manufacture. The average oxygen content of the mounting medium will be lower than that of the epoxy and could be lower in the battery sections than the standards.

As seen in Table 3, the agreement between modal and expected values is good and is not greatly affected by the value assumed for R₀. However, the mean values do depend on R₀. A value of 0.1 was chosen because it gave good agreement between mode and mean for each standard, both being close to the expected value of y = 0. Figure 7 shows a plot of y versus x for standards B and C from which raw totals less than 55% have been rejected and assuming an R₀ value of 0.1. The cluster for standard C is tighter than that for standard B. It is considered that the epoxy mix model is more valid for standard C because of its finer grain size.

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Table 3. Mean and mode of y-values at three values of R₀ for standards B and C.

<table>
<thead>
<tr>
<th>R₀</th>
<th>Mean</th>
<th>Mode</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.267</td>
<td>0.05</td>
<td>0.91</td>
</tr>
<tr>
<td>0.1</td>
<td>0.016</td>
<td>-0.05</td>
<td>0.86</td>
</tr>
<tr>
<td>0.2</td>
<td>-0.238</td>
<td>-0.15</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.435</td>
<td>0.20</td>
<td>0.77</td>
</tr>
<tr>
<td>0.1</td>
<td>0.068</td>
<td>0.15</td>
<td>0.69</td>
</tr>
<tr>
<td>0.2</td>
<td>-0.248</td>
<td>-0.05</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Battery sections and cluster analysis

In Fig. 8 is shown a plot of y versus x for the battery section Y1334. The y values have been calculated using R₀ = 0.1. This battery has been discharged to 0.7 V under the conditions of the 25 S Radio test [1]. There is a large amount of material present containing high levels of zinc (average x = 0.7). The points stream from a possible grouping at (0.15, 2.2) to a cluster at (0.95, 0.8). The first coordinates are consistent with the application of equation 2 to barely converted manganese ore (MnO₂-type) although this is not mathematically correct since MnO₂ is not a hydrohetaerolite-type material. The highly converted material clusters at a y value of about 1.0 and is representative of material approaching Mn₃O₄·ZnO(1+2H₂O). In less deeply discharged batteries having y values between 0.15 and 0.4, the average y values lie between 1.0 and 2.0. Tight clusters are not as evident in scattergrams because x is more variable. It is evident that y decreases generally as the batteries are discharged further. It is not possible to distinguish at this stage between a uniform change in composition (x and y) and a change in the mix of MnO₂ and hydrohetaerolite material at the micrometre level.

Analysis of trace or "tramp" elements

The battery active manganese dioxide ore from Groote Eylandt contains a number of additional oxides [6,7] which could significantly contribute to measured oxygen and hence to errory. Barium, iron, silicon and aluminium occur, the last two in essentially a fixed ratio. The first three have been surveyed and do not cause large errors in y since oxide weight percentages are quite low. It is inferred that this is also true for aluminium oxides. Since only three elements can be measured by WDS in a given survey, manganese is measured in each run along with one or two trace elements.

As seen in Fig. 4, the raw manganese k-ratio is a good predictor of raw total for standard C. This is true for battery section Y1334 for raw totals less than 75%. Hence it is, in a qualitative way, a predictor of grain size. So, by including manganese it is possible to relate trace element levels to grain size, the radial position and the concentration of the third element. A scattergram of barium k-ratio versus Mn k-ratio for the highly discharged battery Y1334 is shown in Fig. 9. Both backgrounds have been measured for barium since it is in low concentration. It is apparent that barium is leached out of the finer material which has lower totals as discussed previously. This has been confirmed by examining the section on the Philips 505 SEM at high magnification. By selecting raw totals less than about 70% (Mn = 42%) but greater than...
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55%, it is found that the barium-depleted material has a mean \((x,y)\) coordinate of \((0.92, 0.70)\) with SD's \((0.17, 0.80)\). It is highly converted, fine-grained material with a \(y\) value close to one. This suggests that Ba becomes mobile in the chloride electrolyte during discharge and on formation of hydrohetaerolite products.

Spatial variations

As Swinkels and Ward [12] noted, no obvious variation in cell chemistry \((x\ or\ y)\) with radial distance has been observed over a set of nine progressively discharged battery sections. With more refined correction procedures or target selection, more subtle variations may become evident. But it appears that the black mix in these batteries is performing well in that the formation of hydrohetaerolite is occurring uniformly throughout the volume of the battery from an early stage in the discharge profile.

Fig. 7. A plot of the calculated \(x\) and \(y\)-values for hetaerolite from a survey of standard \(B\) \((b)\) and standard \(C\) \((c)\). Analyses with totals less than 55 wt.% are not included.

![Graph](image)

Fig. 8. A plot of the calculated \(x\) and \(y\)-values for hetaerolite from a survey of battery plate Y1334. Analyses with totals less than 55 wt.% are not included.

Fig. 9. A plot of the the amount of Ba found in a survey of battery plate Y1334 against the measured Mn-content (wt.%).

Conclusions

It has been shown that even though the material in battery sections is microcrystalline, it is possible to microanalyse the discharge products by collecting a large number of analyses and studying them statistically. Using PAP matrix correction software and a bulk model of the target which includes a correction for the oxygen content of the mounting medium, it is possible to identify the hydrohetaerolite species which develop in cells made from Groote Eylandt manganese ore. No significant variation in the composition of hydrohetaerolite has been found with distance from the centre of these cells.

There are regions in which the pores are not filled with carbon-doped epoxy but the "epoxy mix model" does not account for true porosity of the target. Topography of the oxide grains has not been considered and this together with true porosity contributes to the large spread in \(y\) values when raw totals are low.

Further Work

It had been hoped to use the backscattered signal to provide information on surface irregularities for specific points of analysis but the signal recorded from a symmetrical detector was not found to be useful. In consequence a six-fold detector is being built that allows separate signal processing and it is hoped that these signals will provide more accurate information on surface topography. In addition, direct measurement of carbon is being considered in order to improve the accuracy of partitioning oxygen between oxides and epoxy.

As has been described earlier, the system has the ability to determine particle boundaries. Future work is planned to include a detailed description of the variation in \(x\) and \(y\) within identifiable particle intercepts. Smaller step sizes must be set and many points must be measured but the speed of surveying would be
increased by computing background instead of measuring it. It is expected that greater accuracy in measuring the raw k-ratios will reveal more subtle changes in battery chemistry and the technique will be applied to other battery types.

References


Discussion with Reviewers

G. Rémont: The behaviour of the finely intermixed oxides and epoxy fractions is similar to that of pellets prepared from powders for X-ray Fluorescence Analysis. While in XRF, quantitative data are derived from calibration curves, which are only valid for powders whose grain size remains in a narrow domain, quantitative data with the EPMA are obtained from a model taking account of electron/photon/matter interactions within a single phase. Could the authors briefly summarize the specimen parameters (grain size, lateral and depth distribution of the phases, atomic number differences...) making valid the use of the PAP (or ZAF) model to the study of a target containing several phases within the analysed volume?

Authors: The texture and content of each target in the battery sections is very variable. Grains of hydrohetaerolite are often submicrometre in size and form porous clusters which are flooded wholly or partially with epoxy. Very fine graphite grains or residual carbon black may be mixed in. The analysed volume at 15 kV would be 2-5 µm in diameter so that the target would probably approximate a homogenous matrix with average composition. However, an appreciable amount of material is much coarser. There are grains of porous hydrohetaerolite which probably have unfilled voids and large carbon grains both of which can be several micrometres in diameter. In these cases, the application of PAP for each individual target is not valid but we have assumed that it is valid "on average" over a large number of targets and have tested this on material of known composition. Standard C is the best approximation to the battery material which we could produce, having a grain size of 2 µm or less. We would argue that since the average analysis is good on this standard, the assumption is likely to be valid for the finer battery material. We are unable to perform the difficult task of theoretically modelling such complex material which would be the only other approach. Only in a theoretical study could the effect of grain size and other parameters be thoroughly tested.

G. Rémont: Could the texture of the specimens be modified by the preparatory procedures used (Liquid N₂, vacuum)? Is there any possible influence of texture changes on the validity of the "epoxy mix model"?

Authors: The texture but not the composition of the hydrohetaerolite might be modified by the preparation procedure but since it is not possible to prepare intact sections without freezing in liquid N₂ we cannot check on this. If, in preparation, we are producing a large number of unfilled voids, the "epoxy mix model" would certainly become invalid. We have used a low viscosity epoxy and vacuum impregnation during backfilling because of this possibility.