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Electrochemical study of manganese and iron compounds at carbon paste electrodes with electrolytic binder. Application to the characterization of manganese ferrite

Abstract An electrochemical study of several solids, such as $MnCl_2 \cdot 4\,H_2O_{(s)}$, $MnF_{3(s)}$, $Fe_2O_{3(s)}$, $Fe_3O_{4(s)}$ and $MnO_{2(s)}$, using carbon paste electrodes with electrolytic binders, is described. Results obtained have been compared with results of earlier electrochemical experiments to carry out the characterization of technological material, such as manganese ferrite. The voltammograms obtained represent the "electrochemical spectra" of solid or dissolved substances that can be used to characterize the material without previous solubilization, as charge transfer processes can proceed in the solid or dissolved state, depending on the solubility in the binder used.

Key words Voltammetry · Carbon paste electrode with electrolytic binder · Manganese compounds · Iron compounds

Introduction

A carbon paste electrode was first utilized by R.N. Adams, who used a mixture of carbon paste and organic solvent to study various substances by anodic oxidation or cathodic reduction [1, 2]. Kuwana and French were the first to incorporate electroactive substances into the organic binder [3]. Later, Ruby and Tremmel were the first to electroreduce inorganic solids (4). Alt et al. [5] were the pioneers in using an electrolytic binder for the electrolysis of organic compounds to be used as energy

storage. During the 1970s, several French authors used carbon paste electrodes with electrolytic binder for studying numerous compounds both organic and inorganic [6–19] with this method, formulating the theoretical principles of this electrode. The present authors have studied different compounds of lead, bismuth, iron, tin, copper and selenium, obtaining experimental results illustrating the difference between the intervention of solid and dissolved phases in the electrochemical reactions in this electrode [20–27]. Finally, we must mention the work of F. Scholz et al. [28–34] on a new electranalytical technique, "abrasive stripping analysis", which is related to our work and to that of the French authors in the sense that solid substances are also studied by using electrochemical reactions.

Experimental

Apparatus

Current-potential curves were recorded using an Amel 551 Potentiostat-Galvanostat, an Amel 556 Function Generator and a Linseis X-Y-t recorder.

Electrodes and reagents

A saturated calomel electrode (as a reference electrode), an auxiliary electrode consisting of a Pt wire, and a carbon paste electrode with an electrolytic binder (as a working electrode) were used as has been previously described [20–27]. Carbon powder was spectroscopically pure and was purchased from Carbon of America, Bay City, Michigan State, USA. All reagents were of analytical grade and supplied by Merck and Carlo Erba.

All measurements were carried out with respect to the saturated calomel electrode (SCE).

Procedures

The cavity of the working electrode was filled with a mixture made according to the following procedure: (a) Conducting and pure

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graphite powder (100 mg of ultrapure carbon) plus varying quantities of electroactive substance (between 0.5 and 2 mg) plus the binder consisting of 50 µl of a 10^{-2} M HCl solution were mixed and well ground in an agate mortar; b) Pure graphite (100 mg) plus 50 µl of the electrolytic binder consisting of an acidic extract of the solid sample in a 10^{-2} M HCl solution were added.

The three electrodes were introduced into a classic Metrohm cell with 50 ml of an electrolyte solution of the same nature and concentration as the binder used in the carbon paste preparation. By starting the potential scan from the rest potential value at a scan rate of 0.5 mVs^{-1}, the voltammograms were obtained.

The following electroactive substances were studied: $MnCl_2 \cdot H_2O_{(s)}$, $MnF_{3(s)}$, $MnO_{2(s)}$, $Fe_2O_{3(s)}$, $FeCl_2 \cdot 4 H_2O_{(s)}$, $Fe_3O_{4(s)}$ and $Mn_{0.6}Fe_{2.4}O_{4(s)}$. The electrolyte was a 10^{-2} M HCl solution.

In order to differentiate between electrochemical reactions of dissolved and solid species, different soluble compounds were utilized to prepare our carbon paste electrode.

Results and discussion

### Voltammetric study of Mn(II), Mn(III) and Mn(IV) compounds in a 10^{-2} M HCl medium

Voltammograms of $MnCl_2 \cdot H_2O$

In Fig. 1a, voltammograms are shown which were obtained by electrolyzing 0.6 mg of $MnCl_2 \cdot 4 H_2O$, scanning the potential from +350 mV (rest potential) to −600 mV and then to 1800 mV.

It can be seen in Fig. 1a that in the first cathodic scan no signal appears, but an anodic peak A_1 (developed between 1100 mV and 1600 mV) appears. In the second cathodic scan, between +1800 mV and −600 mV, a cathodic peak C_1 ($E_p \approx +550$ mV) appears. When the potential is scanned, reaching values between +350 mV and +1800 mV, the anodic peak A_1 appears, and finally, between +1800 mV and −600 mV, succes-

sive potential cyclic scans give only the pair of peaks A_1/C_1.

If we repeated the same potential scans, but with an electrode loaded with an extract of 50 µl of $MnCl_2 \cdot 4 H_2O$ in a 10^{-2} M HCl solution, the obtained voltammograms were identical to those in Fig. 1a, b. These results indicate that the pair of peaks A_1/C_1 corresponds to the electrochemical reactions of the following soluble redox couple present in the interstitial solution:

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e$$
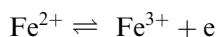
Voltammograms of $MnF_{3(s)}$

When 0.7 mg of this solid was electrolyzed, by starting the potential from +950 mV (rest potential), first down to −600 mV then up to +1800 mV and then cycling, the voltammograms plotted in Fig. 2a, b were obtained.

If the first scan is expanded towards −600 mV (Fig. 2a) the peak C_2 (−50 mV) appears and in the anodic scan the peak A_1 is obtained. In the second cathodic scan peaks, C_1 and C_2 appear. In Fig. 2b, peak A_1 appears in the first potential scan and peaks C_1 and C_2 during the back scan. Peak C_2 disappears in the third cyclic potential scan. After the third scan, only peaks A_1 and C_1 remain.

When potential scans are carried out between −600 mV and +1100 mV, voltammograms in which only the peak C_2 is observed are obtained. Later, this peak also disappears.

Voltammograms obtained with carbon paste electrodes in which the binder is formed by a saturated solution of $MnF_{3(s)}$ in a 10^{-2} M HCl solution are identical to those in Fig. 1a, b.

Fig. 1a, b Voltammograms of 0.6 mg of $MnCl_2 \cdot 4 H_2O_{(s)}$ in a 10^{-2} M HCl solution recorded at 0.5 mV s^{-1} E_R = +350 mV, **a** towards −600 mV, and **b** towards +1800 mV. *Solid lines* correspond to first potential scans, and *dotted lines* to cyclic potential scans
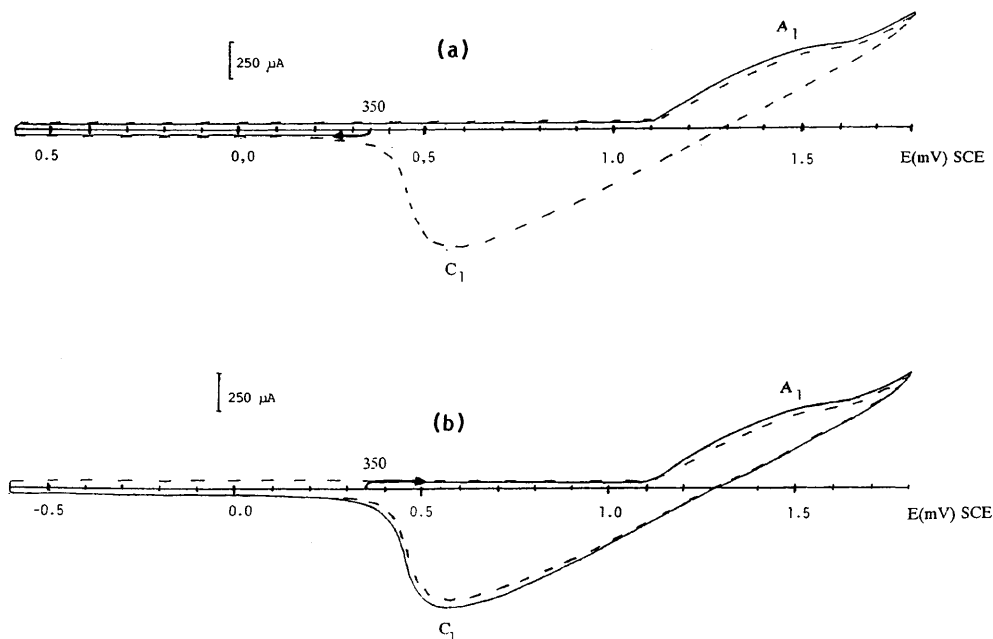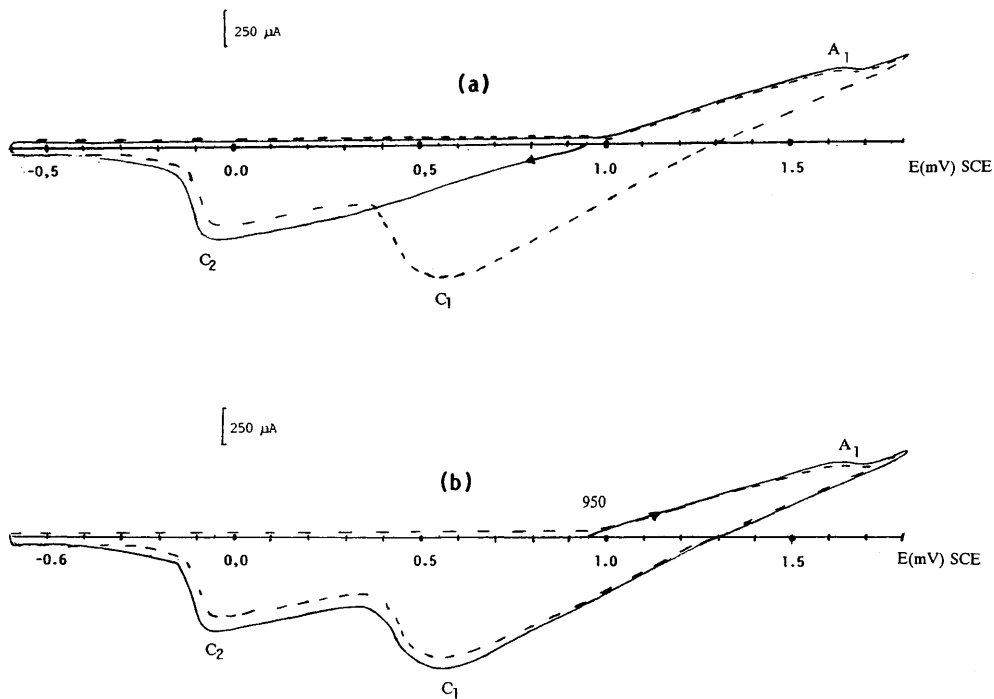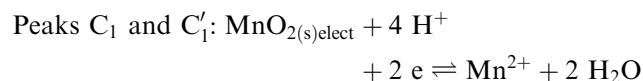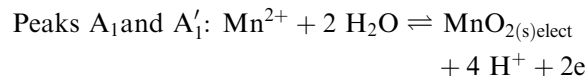
Fig. 2a, b Voltammograms of 0.7 mg of $MnF_{3(s)}$ in a 10^{-2} M HCl solution recorded at 0.5 mV s^{-1}, $E_R = +950$ mV, **a** towards -600 mV, and **b** towards $+1800$ mV. *Solid lines* correspond to first potential scans, and *dotted lines* to cyclic potential scans

Voltammograms of $MnO_{2(s)}$

Figure 3 corresponds to voltammograms obtained by electrolyzing 2 mg of $MnO_{2(s)}$ and carrying out the potential scan between -600 mV and 1800 mV, starting from $+750$ mV. When the first scan is carried out in the cathodic direction (Fig. 3a), peak C_3 ($+350$ mV) appears, and in the anodic scan, the obtained peak is A_1. In the second cathodic scan, peak C_1 appears and peak C_3 disappears. In Fig. 3b, in which the potential is scanned to $+1800$ mV, the small peak A'_1 ($+1370$ mV) is observed during the first anodic scan as well as peaks C'_1 and C_3 in the first cathodic scan. In both cases, only peaks A_1 and C_1 appear in the cyclic potential scans. If the potential is scanned between -600 mV and $+1100$ mV, a voltammogram is obtained in which only peak C_3 appears. Further cyclic scans do not give any signal. Figure 3c corresponds to voltammograms obtained with carbon paste electrodes in which the binder is formed by 50 μl of an extract of $MnO_{2(s)}$ in a 10^{-2} M HCl solution.

In all experiments carried out with the three manganese compounds, a brown deposit appeared on the Pt contact of the working electrode when the potential was scanned up to $+1800$ mV. This is important.

From the experimental results, it can be deduced that the different peaks correspond to the following electrochemical reactions:

Peaks A_1 and A'_1: $Mn^{2+} + 2\,H_2O \rightleftharpoons MnO_{2(s)elect}$
$$+ 4\,H^+ + 2e$$

Peaks C_1 and C'_1: $MnO_{2(s)elect} + 4\,H^+$
$$+ 2\,e \rightleftharpoons Mn^{2+} + 2\,H_2O$$

The proposed oxidation process is based on the appearance of the brown deposit on the Pt contact of the working electrode; the obtained $MnO_{2(s)elect}$ is named "electrolytic manganese dioxide", as the oxidation of Mn(II) salts in acidic media never gives stoichiometric forms of this oxide [35].

The electrochemically obtained oxide can be subsequently reduced at different potentials to reduced $MnO_{2(s)}$, which also can be obtained by other procedures.

The peak C_2, which is observed only when $MnF_{3(s)}$ is present, is assigned to the following electrochemical reaction:

$$MnO_{2(s)dism} + 4\,H^+ + 2\,e \rightarrow Mn^{2+} + 2\,H_2O$$
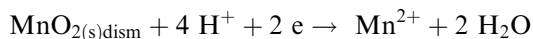
because $MnO_{2(s)dism}$ is due to the previous chemical reaction, that is to say where

$$2\,Mn^{3+} + 2\,H_2O \rightarrow Mn^{2+} + MnO_{2(s)dism} + 4\,H^+$$
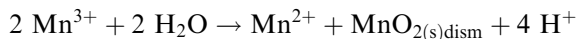
are produced when the medium is not sufficient acidic [36]. $MnO_{2(s)elect}$ and $MnO_{2(s)dism}$ are solid produced by electrochemical reaction and chemical dismutation respectively.

The $MnO_{2(s)}$ which cannot correspond to the stoichiometric forms of this oxide [37, 38] is reduced at peak C_2. The Mn^{2+} which is present in the electrode because of the dismutation process is oxidized at peak A_1.

The peak C_3 appears only during the first cathodic scan, when commercial $MnO_{2(s)}$ is introduced into the carbon paste electrode. It is due to the following electrochemical reaction:
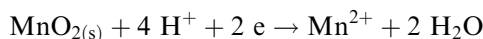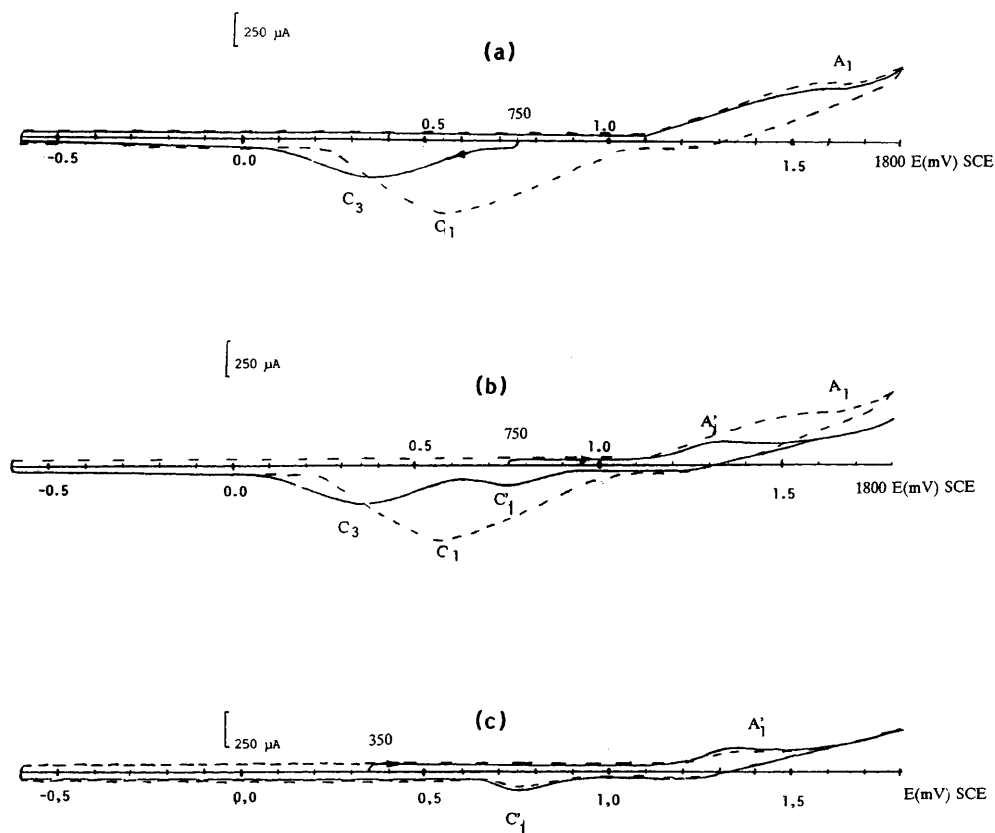
$$MnO_{2(s)} + 4\,H^+ + 2\,e \rightarrow Mn^{2+} + 2\,H_2O$$

Fig. 3a–c Voltammograms recorded at 0.5 mV s^{-1} of 2 mg of MnO$_{2(s)}$ in a 10^{-2} M HCl solution, E_R = +750 mV, **a** towards −600 mV, and **b** but towards +1800 mV. **c** Voltammogram of 50 μl of an acidic extract of MnO$_{2(s)}$ in a 10^{-2} M HCl solution, from E_R = +350 mV towards +1800 mV. *Solid lines* correspond to first potential scans, *dotted lines* to cyclic potential scans

because this oxide can occur in an allotropic form different from MnO$_{2(s)elect}$ and MnO$_{2(s)dism}$, hence giving different reduction potentials. These results are in accord with those of other authors [39, 15].

Voltammetric study of Fe(II) and Fe(III) compounds in a 10^{-2} M HCl medium

In other papers [25, 26], several studies of Fe(II) and Fe(III) compounds in a 1 M HCl medium have been described. However, in order to know the behavior of these compounds in more weakly acid media, voltammograms of FeCl$_2 \cdot 4$ H$_2$O$_{(s)}$, Fe$_2$O$_{3(s)}$ and Fe$_3$O$_{4(s)}$ were obtained with a carbon paste electrode with 50 μl of a 10^{-2} M HCl solution as binder (Fig. 4).

By scanning the potential from the rest potential value (+410 mV) to −600 mV, no signal was obtained (Fig. 4a). In the anodic scan between −600 mV and +1800 mV, the peak A$_2$ appears, and finally, by cyclic scanning between +1800 mV and −600 mV, only the pair of peaks A$_2$/C$_4$ was obtained.

Using a carbon paste electrode loaded with Fe$_2$O$_{3(s)}$ and scanning the potential from +330 mV (rest potential) to −600 mV, the cathodic peak C$_5$ was obtained, while by scanning the potential between −600 mV and +1800 mV, the anodic peak A$_2$ was obtained. Then, cycling between +1800 mV and −600 mV, only the peak pair of peaks A$_2$/C$_4$ was obtained. These peaks can be seen in Fig. 4b.

Finally, by loading the carbon paste electrode with Fe$_3$O$_{4(s)}$ (magnetite), using a 10^{-2} M HCl solution and scanning from +350 mV (rest potential) to −600 mV, the cathodic peak C$_6$ was obtained (Fig. 4c). Between −600 mV and 1800 mV one peak only, A$_2$, was obtained. Finally, by scanning between +1800 mV and −600 mV only the pair of peaks A$_2$/C$_4$ was obtained (Fig. 4c).

Peak A$_2$: Fe^{2+} → Fe^{3+} + e

Peak C$_4$: Fe^{3+} + e → Fe^{2+}
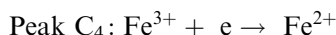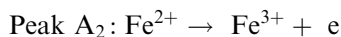
The peak C$_5$, which only appears in the first cathodic potential scan when Fe$_2$O$_{3(s)}$ is present in the electrode, is the result of the following electrochemical reaction:
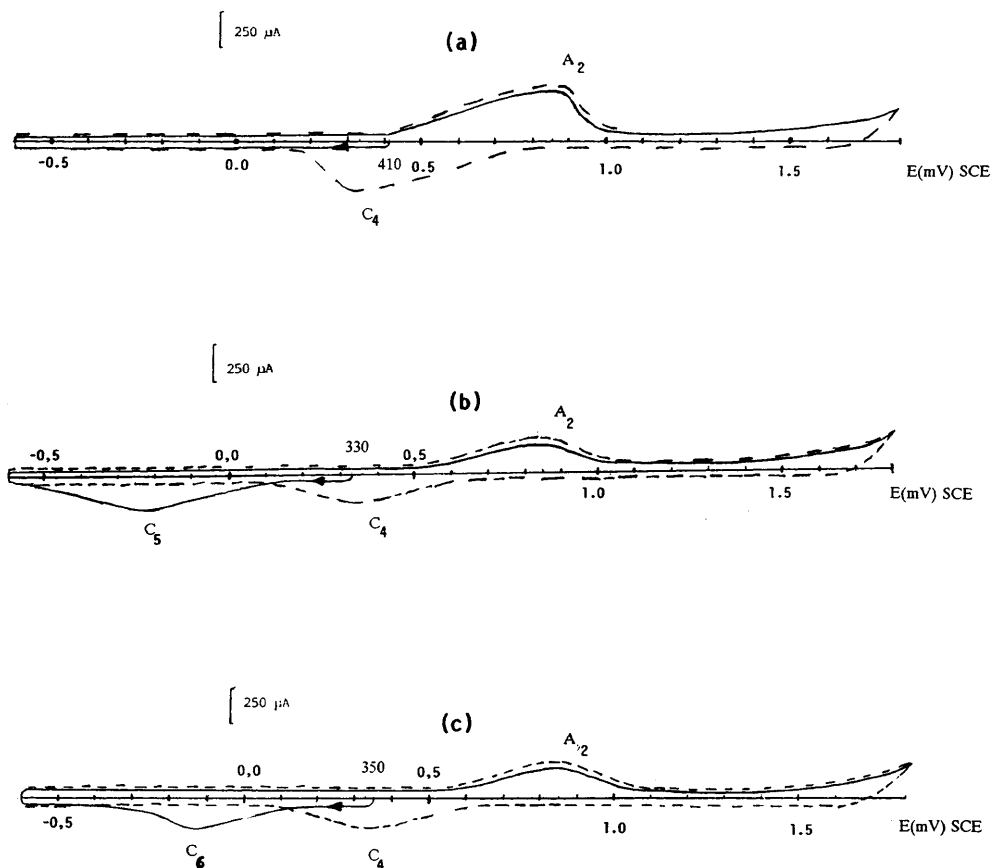
Fe$_2$O$_{3(s)}$ + 6 H$^+$ + 2 e → 2 Fe^{2+} + 3 H$_2$O
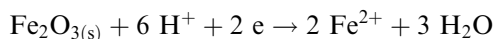
The peak C$_6$, that only appears in the first cathodic scan when Fe$_3$O$_{4(s)}$ is introduced into the electrode, is due to the following electrochemical reaction:

Fe$_3$O$_{4(s)}$ + 8 H$^+$ + 2 e → 3 Fe^{2+} + 4 H$_2$O
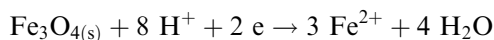
Voltammetric study of binary mixtures of manganese and iron compounds in a 10^{-2} M HCl medium

In order to characterize solid manganese ferrite using voltammetric techniques with carbon paste electrodes,

different binary mixtures of manganese and iron were studied. Voltammograms were obtained in all cases by scanning the potential between −600 mV and +1800 mV, starting the potential scan from the rest potential.

Voltammograms of MnCl$_2$ · 4 H$_2$O$_{(s)}$ + various iron compounds

In Fig. 5 voltammograms corresponding to three mixtures studied are shown. The two pairs of peaks A$_1$/C$_1$ and A$_2$/C$_4$ correspond to manganese and iron (Fig. 5a). In Fig. 5b the peak C$_5$, which is characteristic of Fe$_2$O$_{3(s)}$, appears, and in Fig. 5c the peak C$_6$ corresponding to Fe$_3$O$_{4(s)}$ also appears.

Taking into account that well-distinguishable peaks appear, we conclude that it is possible to identify every compound in these solid mixtures.

Voltammograms of MnF$_{3(s)}$ + various iron compounds

Voltammograms of three mixtures are depicted in Fig. 6. In all cases, the peak pairs A$_1$/C$_1$ and A$_2$/C$_4$ corresponding to the manganese and iron compounds, respectively, are well developed.

In Fig. 6a, the peak C$_2$ appears, which corresponds to the electrochemical reduction of MnF$_3$, whereas in Fig. 6b and Fig. 6c, this peak overlaps with C$_5$ which is due to the electrochemical reduction of Fe$_2$O$_{3(s)}$, or with peak C$_6$ corresponding to the electrochemical reduction of Fe$_3$O$_{4(s)}$, respectively. Therefore, it is not possible to distinguish between Fe$_2$O$_{3(s)}$ and Fe$_3$O$_{4(s)}$ by using this method, although the presence of Mn(II) as well as that of Fe(III) or Fe(II) can be confirmed by a simple potential scan in the anodic direction.

Voltammograms of MnO$_{2(s)}$ + various iron compounds

Figure 7 corresponds to the three mixtures studied.

Here, the presence of the two voltammetric systems A$_1$/C$_1$ and A$_2$/C$_4$ is observed. Also, the characteristic peaks C$_3$, C$_5$ and C$_6$, corresponding to MnO$_{2(s)}$, Fe$_2$O$_{3(s)}$and Fe$_3$O$_{4(s)}$, respectively, appear well separated. Therefore, the presence of each compound in these mixtures is confirmed.

Voltammetric study of manganese ferrite, Mn$_{0.6}$Fe$_{2.4}$O$_{4(s)}$, in a 10^{-2} M HCl medium

Voltammograms obtained by scanning the potential between −600 mV and +1800 mV, starting from +360 mV, are shown in Fig. 8.

Fig. 5a–c Voltammograms of $MnCl_2 \cdot 4\,H_2O_{8(s)}$ + various iron compounds: **a** 0.7 mg of $MnCl_2 \cdot 4\,H_2O_{(s)}$ +0.7 mg of $FeCl_2 \cdot 4\,H_2O_{(s)}$, $E_R = +370$ mV, **b** 0.7 mg of $MnCl_2 \cdot 4\,H_2O_{(s)}$ +0.7 mg of $Fe_2O_{3(s)}$, $E_R = +330$ mV, and **c** 0.7 mg of $MnCl_2 \cdot 4\,H_2O$ +0.7 mg of $Fe_3O_{4(s)}$, $E_R = +350$ mV. *Solid lines* correspond to first potential scans, *dotted lines* to cyclic potential scans
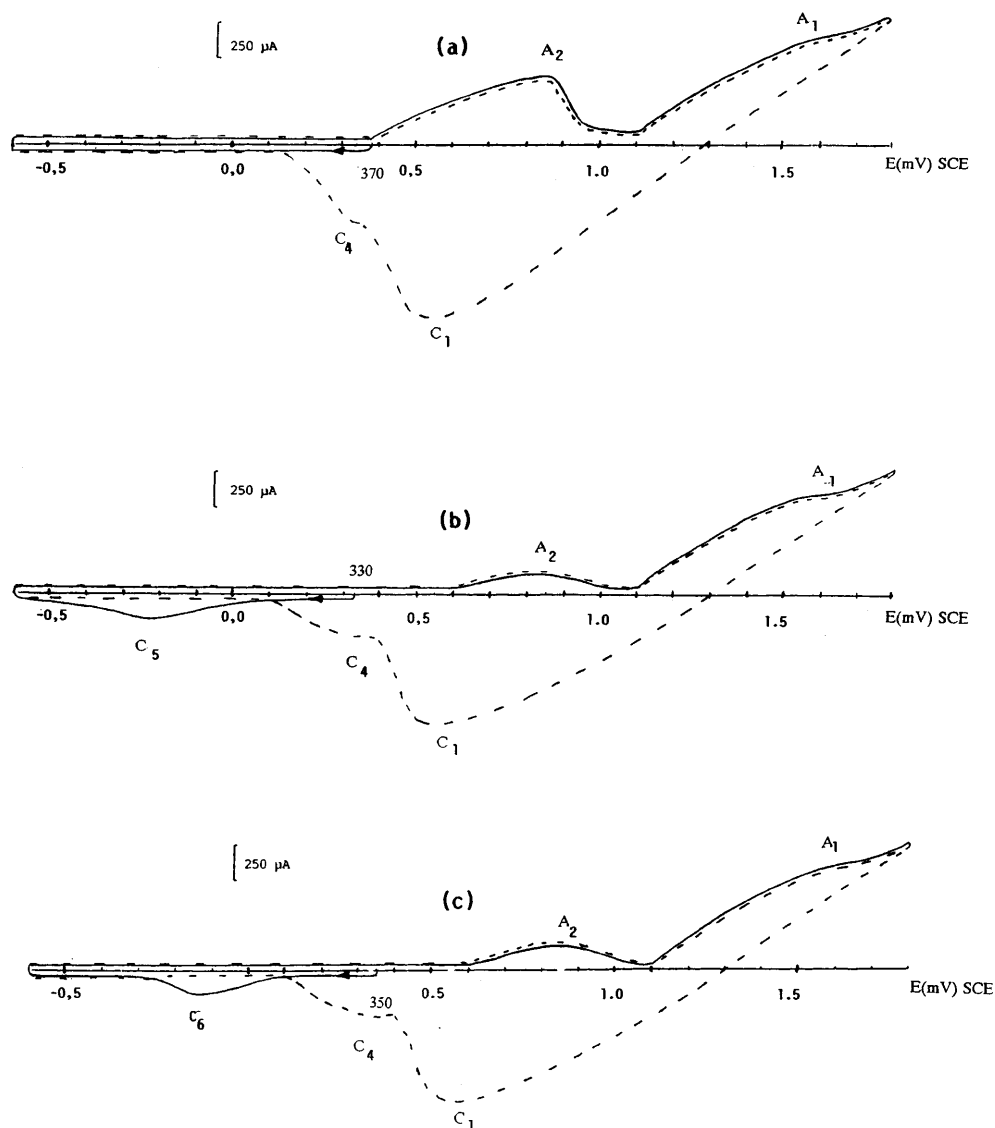
When the first potential scan is carried out towards −600 mV, the broad peak L_1 (with a maximum at −150 mV) is obtained. In the anodic potential scan, peaks M_1 (+850 mV) and M_2 (+1600 mV) are obtained, and, in the second cathodic potential scan, only the peaks L_2 (+550 mV) and L_3 (+330 mV) are observed. In successive cyclic scans, the anodic peaks M_1 (+850 mV) and M_2 (+1600 mV) and the cathodic peaks L_2 and L_3 are obtained (Fig. 8a).

Figure 8b shows the voltammogram obtained by scanning the potential in the anodic direction to +1800 mV, then to cathodic potentials up to −600 mV, and then cycling between these two potentials. No signal appears in the first anodic potential scan, and only the peak L_1 (−150 mV) appears in the first cathodic potential scan. In the cyclic scan, only the anodic peaks M_1 and M_2 and the cathodic peaks L_2 and L_3 appear. If the potential scan is carried out between −600 mV and +1100 mV, only the peak L_1 is observed in the first

cathodic scan, and peaks M_1 and L_3 are present in the subsequent cyclic scans.

Voltammograms obtained with electrodes in which the binder is formed by saturated extracts of manganese ferrite in a 10^{-2} M HCl solution did not give any signal.

By comparing voltammograms of solid ferrites with those corresponding to the different mixtures, we deduce the following:

(a) The voltammogram obtained when a first cathodic scan is performed (Fig. 8a), shows an electrochemical profile very similar to that given by the following mixtures:

$Fe_2O_{3(s)}$ + $MnCl_2 \cdot 4\,H_2O_{(s)}$ (Fig. 5b)
and $Fe_3O_{4(s)}$ + $MnCl_2 \cdot 4\,H_2O_{(s)}$ (Fig. 5c).
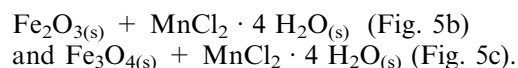
Because no signal is observed at potential values near −50 mV and +350 mV (potential values

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Fig. 6a–c Voltammograms of $MnF_{3(s)}$ + various iron compounds: **a** 0.7 mg of $MnF_{3(s)}$ +0.7 mg of $FeCl_2 A 4 - H_2O_{(s)}$, $E_R = +420$ mV, **b** 0.7 mg of $MnF_{3(s)}$ +0.7 mg of $Fe_2O_{3(s)}$, $E_R = +840$ mV, and **c** 0.7 mg of $MnF_{3(s)}$ +0.7 mg of $Fe_3O_{4(s)}$, $E_R = +900$ mV. *Solid lines* correspond to first potential scans, *dotted lines* correspond cyclic potential scans
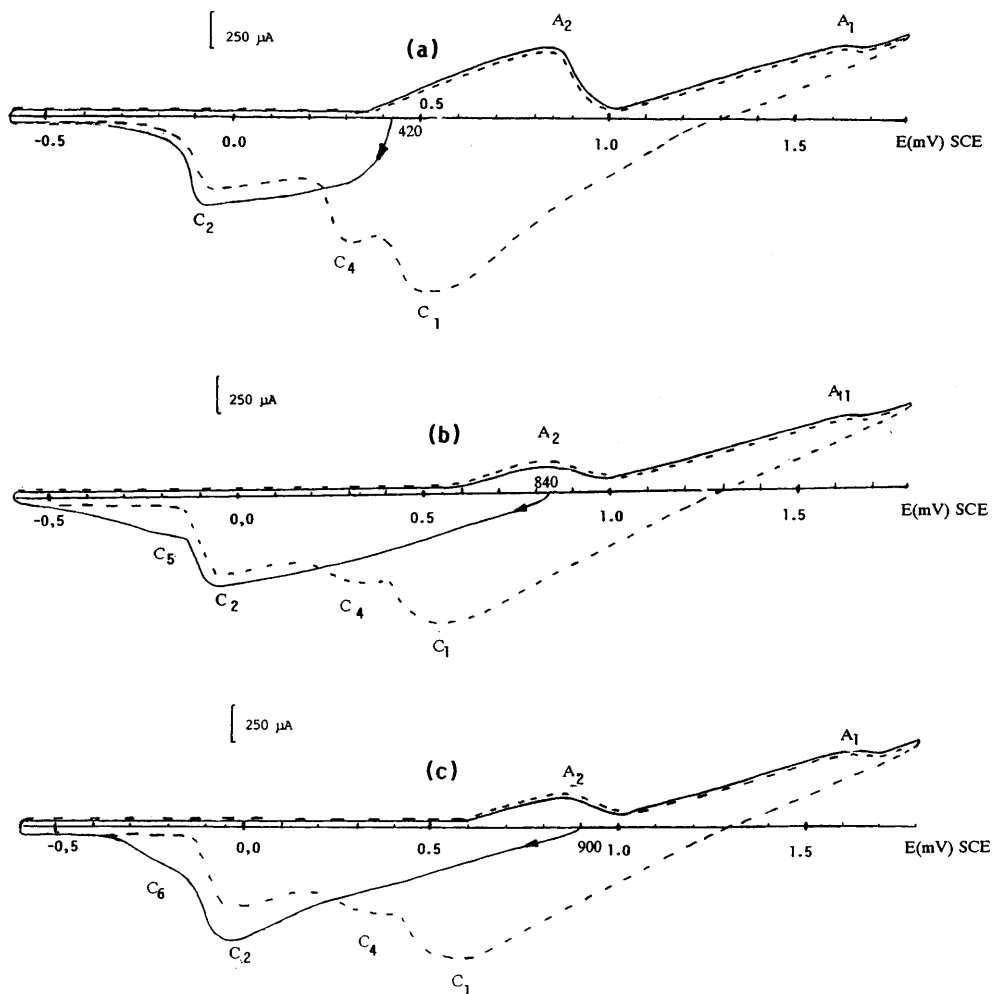
corresponding to the peaks C_2 and C_3 for Mn(III) (Fig. 6a, b, c) and for Mn(IV) (Fig. 3a, b), respectively, and the peak L_1 (Fig. 8a, b) does not show any disturbance caused by overlapping, it can be deduced that these species are not present in the solid ferrite or that their identification is not possible by this technique. However, the peak L_1, which only appears in the first cathodic scan, confirms the presence of Fe(III).

(b) In contrast, when the potential is first scanned in the anodic direction, the voltammogram of the ferrite is not similar to the one obtained in the case of the different mixtures, because no signal is shown in the first potential scan and peaks M_1 and M_2 appear. These results did not enable us to determine the degree of oxidation of Mn in the ferrite, because the characteristic peak M_2 of Mn(II) in solution is only observed after the ferrite is reduced.

Different ferrites were recently studied by T. Grygar [42], using the stripping abrasive voltammetry (SAV) technique. Poorer voltammograms were obtained than those obtained by us, and yet these were very interesting

because they enable electrochemical profiles of solids only to be obtained, because, taking into account the electrode design, the ions produced in the electrochemical reactions diffuse towards the solution and are not detected. On the contrary, our method is very appropriate, qualitatively speaking, for differentiating, at the same time, between the electrochemical reactions of solid and dissolved species, because of the special design of our carbon paste electrodes. This is the main reason for adding to our electrode, in many cases, soluble substances, only from an analytical point of view, in the case of solid studies.

Conclusions

In conclusion, we can confirm that it is possible to characterize electrochemically different manganese and iron compounds by using voltammetric techniques using carbon paste electrodes with an electrolytic binder and incorporated electroactive compounds. It is also possible to identify different species present in binary mixtures.

Fig. 7a–c Voltammograms of
$MnO_{2(s)}$ + various iron com-
pounds: a 0.7 mg of $MnO_{2(s)}$
+0.7 mg of $FeCl_{2(s)} \cdot 4 H_2O_{(s)}$,
$E_R = +510$ mV, b 0.7 mg of
$MnO_{2(s)}$ +0.7 mg of $Fe_2O_{3(s)}$,
$E_R = +730$ mV, and c 0.7 mg of
$MnO_{2(s)}$ +0.7 mg of $Fe_3O_{4(s)}$,
$E_R = +750$ mV. Solid lines cor-
respond to first potential scans,
dotted lines to cyclic potential
scans

Fig. 8a, b Voltammograms of
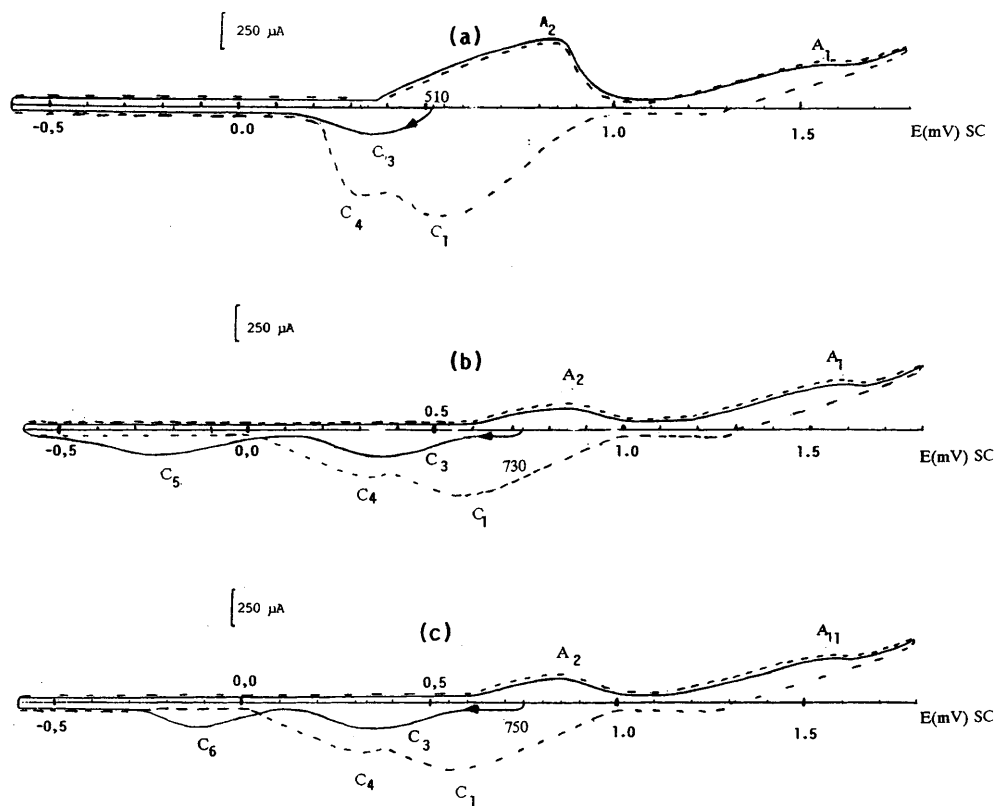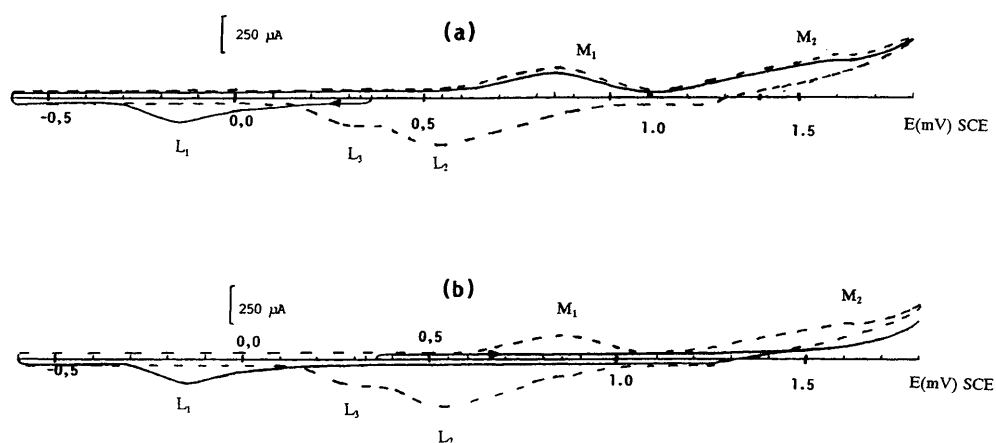2 mg of manganese ferrite, Mn_6
$Fe_{24}O_{40(s)}$, $E_R = +360$ mV, a
towards negative values and b
towards positive values. Solid
lines correspond to the first po-
tential scan, dotted lines to cyclic
potential scans

The application of this method to the case of manganese ferrite only enables the presence of Fe(III) to be confirmed.

The results obtained support the hypothesis already mentioned in other papers that the direct interconversion of solid in materials is possible in cathodic-anodic processes at the carbon paste electrode with an electrolytic binder.

These electrochemical processes give characteristic voltammograms, which, although corresponding to electrochemical transformations of solids or dissolved species of the same chemical nature, provide different shapes and potentials.

The poor shapes of voltammograms are probably due to several causes: (1) poor solubility of solid in the binder utilized, (2) poor conductivity of solids, etc. This confirms our findings, submitted to other journals [40, 41], concerning the influence of concentration and composition of the binder on voltammetric curves obtained using carbon paste electrodes with electrolytic binder.

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