



Copper deoxidation with calcium carbide melts: electrochemical reactions

E. KRASICKA-CYDZIK¹, D. INMAN² and R.V. KUMAR³

¹Department of Mechanical Engineering, Technical University of Zielona Gora, Poland

²Department of Materials, Imperial College of Science, Technology and Medicine, Great Britain

³Department of Materials Science and Metallurgy, University of Cambridge, Great Britain

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Abstract

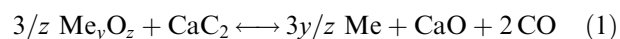
Molten copper containing variable quantities of oxygen up to the saturation concentration 0.8 wt % O can be effectively deoxidized by calcium chloride melts containing 5 wt % calcium carbide. Cyclic voltammetry, on solid copper electrodes in this melt at a temperature of 1073 K, revealed the reaction responsible for copper deoxidation, namely, the electrochemical oxidation of the carbide ion C_2^{2-} .

1. Introduction

Slag/metal reactions involve the transport of chemical species to and from the interface as well as transfer across the interface. The latter process is usually associated with charge transfer. This process is often fast so that the slag/metal reactions are transport-controlled in real conditions. Many refining reactions in extractive metallurgy, such as metal recovery from slags and scrap, involve the reduction of copper oxides. Hence, the rate constants for the deoxidation of copper and/or reduction of copper ions, enter into the overall rate constant of the refining process. For investigations of the kinetics and mechanisms of the process, the most common method consists of sampling the liquid metal during refining, to provide information on changes of impurity concentration. However, the evaluation of metal quality in this case can only be made *post priori*. Hence, the possibility of controlling the online properties of liquid metal is of great importance in industry. Liquid copper, with variable amounts of oxygen and sulfur (up to the saturation concentration 0.8 wt % O), was effectively deoxidized and desulfurised [1, 2] at the temperature 1473 K by solid calcium carbide (technical grade) and calcium carbide dissolved in a molten salt, using an imposed direct current (current density $1 \times 10^{-4} \text{ A m}^{-2}$). After 900 s of treatment the final concentrations of oxygen and sulphur were reduced to levels of 80 ppm and 9 ppm, respectively.

1.1. Application of calcium carbide in extractive metallurgy

If the general reaction [1] between calcium carbide and metal oxide:



is applied to the reduction of cupric oxide



then the values of standard free energy at 1500 K calculated [3] for the above reactions are

$$\Delta G_{1500\text{K}}^\circ(2) = -665 \text{ kJ mol}^{-1} \text{ O}_2$$

$$\Delta G_{1500\text{K}}^\circ(3) = -358 \text{ kJ mol}^{-1} \text{ O}_2$$

which confirms the favourable conditions for cupric oxide reduction due to Reaction 2.

1.2. Properties of calcium carbide

A typical composition of technical grade calcium carbide is as follows (wt %): calcium carbide (CaC_2) 75.00; calcium oxide (CaO) 20.00; magnesium oxide (MgO) 0.06; silicon dioxide (SiO_2) 2.64; aluminium oxide (Al_2O_3) 1.10; iron oxide (Fe_2O_3) 0.70; carbon (C) 0.40; and sulfur (S) 0.05.

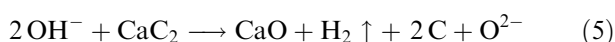
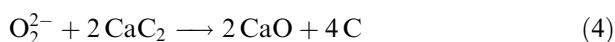
According to Geld et al. [4] liquid calcium carbide is a strong, ionic electrolyte of resistivity from 0.2 to $2 \times 10^{-2} \Omega \text{ m}$ at 2123 K. The carbide ions play the same role as the anions containing silicon and aluminium in silica and alumina slags. As a result, the calcium ions become the main charge carriers. For comparison, the resistivities of some other molten salts are:

NaCl	$0.26 \times 10^{-2} \Omega \text{ m}$	1223 K
$\text{Na}_2\text{O} \cdot x \text{SiO}_2$	$5.8 \times 10^{-2} \Omega \text{ m}$	1373–1473 K
Slags	$0.1\text{--}2 \times 10^{-2} \Omega \text{ m}$	1373–1573 K
CaCl_2	$0.38 \times 10^{-2} \Omega \text{ m}$	1239 K
CaF_2	$0.25 \times 10^{-2} \Omega \text{ m}$	1696 K

It is interesting that Mitchell and Cameron reported [5] a decrease in the resistivity of slags after the addition of calcium carbide. However, as previously mentioned [6], this could result from the precipitation of carbon above the value of decomposition potential, which according to the authors' calculation is about 0.490 V.

1.3. Carbide containing melts

In the earliest works [7–12] with solutions of carbide in melts, halides of alkali metals were suggested as suitable solvents for calcium carbide. According to Geld and Jesin [7] carbide dissolved at lower temperatures in the presence of active halide anions. Barber and Sloane [8] suggested CaCl_2 , LiF, LiBr and BaCl_2 as effective solvents for carbide. White, Morris et al. [9, 10] and Bonomi et al. [11, 12] used calcium chloride alone or in eutectic mixtures with lithium, sodium or barium chlorides, in their investigations on calcium carbide cells. However, the disadvantages of calcium chloride with regard to cells are its hygroscopic properties. This leads to melt contamination with O^{2-} , O_2^{2-} and OH^- . Such a possibility was reported by Brooks and Inman [13, 14] and Melendres et al. [15], although White [9] reported that the carbide ion itself could be a factor eliminating this risk according to the reactions:



Most carbide melt studies, listed in Table 1, have focussed on measurements of emf [10, 16] and the investigation of steel carbonisation [10, 12, 17]. Barber

[8] and Morris et al. [10] found that, on average, 15 wt % of calcium carbide was sufficient to saturate calcium chloride at 1000 K. However, when adding carbide particles (0.8–2 mm dia.) in small portions, it was possible to dissolve about 25 wt % of the reagent in calcium chloride solution [3, 17]. Many investigators, in explaining the operation of the investigated electrochemical cells, chose, as Bonomi et al. [11], the carbide formation reaction as that responsible for the cell behaviour, while Morris et al. [10] suggested the following scheme: $\text{Fe}(\text{C})/\text{Ca}_{(\text{ac}')} , \text{CaC}_2, \text{CaCl}_2, \text{Ca}_{(\text{ac}')} / \text{C}$ for their cells.

Many efforts undertaken to melt the calcium carbide, in order to use it as a reagent in extractive metallurgy and in grain refinement processes for copper, brasses and bronzes [18–21], identified the usefulness of the following components: Na_2CO_3 , $\text{Na}_2\text{B}_4\text{O}_7$, B_2O_3 , CaF_2 , NaF and NaCl. However, CaCl_2 was the most promising.

When considering the chemical composition of the electrolyte and slag, for the above refining systems, the following ions can be assumed to be present: Ca^{2+} , C_2^{2-} , Cl^- , O^{2-} , Cu^{2+} and Cu^+ . To identify relationships between copper and molten salt mixtures containing calcium carbide, the investigations focussed on Reaction 2 for solid copper.

2. Experimental details

Cyclic voltammetry was the electrochemical technique chosen to investigate the calcium chloride/calcium oxide/calcium carbide system. It should be emphasized that, given the inherent experimental difficulties encountered in working with molten salts at high temperatures, the technique has been applied in a quasi-quantitative manner relative to that of the rigorous technique that has now been developed for, mainly, aqueous solutions. Thus such matters as peak deconvolution, solvent background subtraction etc. have not been addressed. The conclusions of this work should therefore be regarded as tentative.

Table 1. Studies of calcium carbide melts

Scheme of cell	Reactions	Parameters	Reference method
Fe, Li–Ca/LiCl– $\text{CaCl}_{2\text{eut}}$, CaC_2/C , Fe	$\text{Ca}_{\text{Li-Ca}} + 2 \text{C} \rightarrow \text{CaC}_2$	823–973 K sat. CaC_2	[11], potentiometry
$\text{C}/\text{CaCl}_2, \text{CaC}_2/\text{C}$	$\text{Ca}^{2+} + 2 \text{e}^- \rightarrow \text{Ca}$ $\text{C}_2^{2-} \rightarrow 2 \text{C} + 2 \text{e}^-$ $\text{Ca} \leftrightarrow \text{Ca}^{2+} + 2 \text{e}^-$ $\text{O}^{2-} \rightarrow [\text{O}] + 2 \text{e}^-$ $[\text{O}] + \text{C} \rightarrow \text{CO}$	890 K CaC_2	[19], e.m.f. chronopotentiometry
Fe, $\text{C}/\text{CaCl}_2, \text{CaC}_2/\text{C}$	$\text{CaC}_2 \leftrightarrow \text{Ca} + 2 \text{C}$ $\text{Ca} \leftrightarrow \text{Ca}^{2+} + 2 \text{e}^-$	1073–1273 K sat. CaC_2	[10] e.m.f.
Fe, $\text{C}/\text{CaCl}_2, \text{CaC}_2/\text{C}$	$\text{C}_2^{2-} \rightarrow 2 \text{C} + 2 \text{e}^-$ $\text{Ca}^{2+} + 2 \text{e}^- \rightarrow \text{Ca}$	920 °C, 4,76 wt % CaC_2	[12], chronopotentiometry
Li/Li–KCl, LiCl/C	$\text{C}_2^{2-} \leftrightarrow 2 \text{C} + 2 \text{e}^-$	660–850 K	[16] e.m.f., cyclic voltammetry

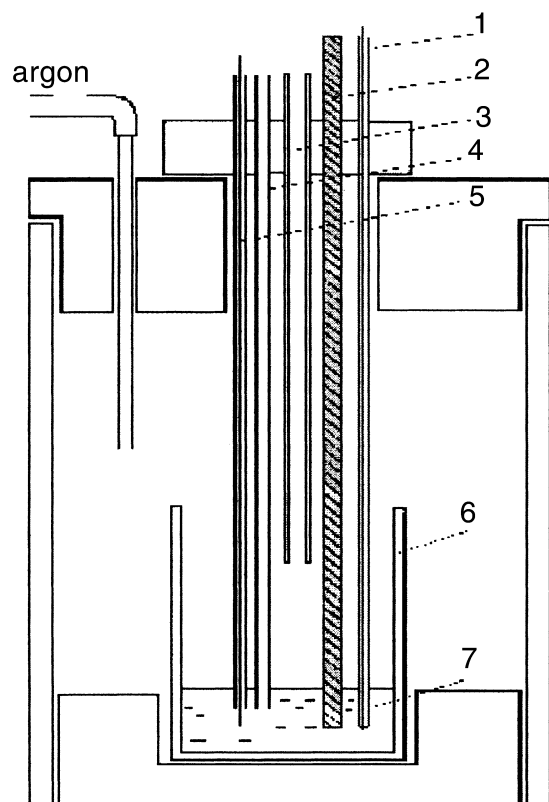


Fig. 1. Electrochemical cell for studies copper deoxidation in calcium carbide melts. Key: (1) thermocouple, (2) graphite counter electrode, (3) addition tube, (4) copper working electrode, (5) tungsten reference electrode, (6) alumina crucible, and (7) calcium carbide melt.

The cyclic voltammetry experiments were performed in the three-electrode manner in an alumina crucible (100 mm depth, 50 mm inner dia.). The electrochemical cell is shown in Figure 1. A copper rod of diameter 2 mm, 10–15 mm depth in the melt, was used as the working electrode and a graphite rod (5 mm dia.) as the

counter electrode. Tungsten rods (1 mm dia.) and 99.999% pure copper (2 mm dia.) rods, both 30 mm depth in the electrolyte, as well as platinum wire (0.5 mm dia., 100 mm length), all inserted in alumina tubes, were examined in separate experiments as quasi-reference electrodes. Figure 2 shows the values of potential against time for the three different materials. The most stable potential was observed for the tungsten rod, which was eventually applied as a quasi-reference electrode in the main experiments. To eliminate the iR drop in the melt, two electrodes: a tungsten quasi-reference electrode (QRE) and a copper working electrode (WE) were placed inside alumina tubes of diameter 5 mm and fixed in contact with each other in the cover of the crucible. Thus, the distance between these two electrodes was no larger than 5 mm, in order to significantly decrease the influence of iR drop.

The electrolyte was prepared from dehydrated pure calcium chloride (99.9% Aldrich) and technical grade calcium carbide powder, by remelting first calcium chloride in a resistance furnace at about 1000 K under an argon atmosphere to remove moisture, and then adding 5 wt % calcium oxide. After cooling, it was kept in a gas-tight, glass container. Portions of 2, 5 and 10 wt % of calcium carbide were then added sequentially to the previously prepared calcium chloride melts through an addition tube just before the voltammetric experiments. A larger quantity of calcium carbide, 15 wt %, was also used, but without the addition of calcium oxide in order not to change the melting points of the mixtures. Equilibration of the system took between 900–3600 s, depending on the quantity of calcium carbide added, after which the external voltage was applied by the PAR 273 and data were registered with the X-Y recorder. All voltammetric investigations were performed in a sealed chamber of a resistance furnace which was continuously purged with argon ($\sim 200 \text{ ml min}^{-1}$).

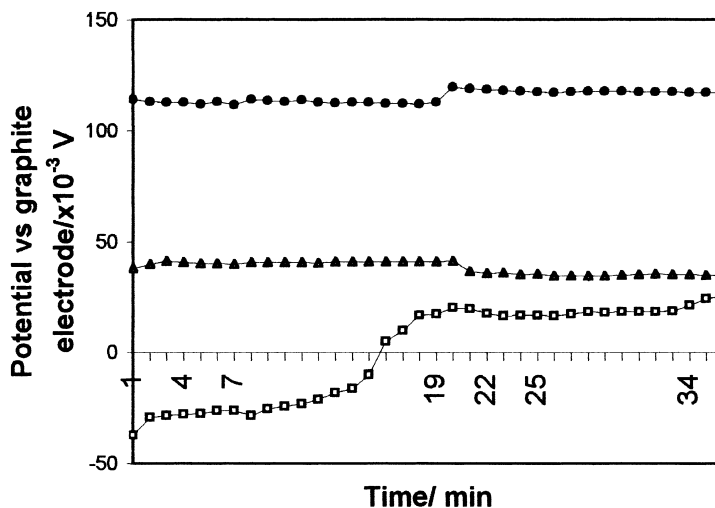


Fig. 2. Potential against time for reference materials. Key: (□) Pt 1 mm wire; (●) W 1 mm rod; (▲) Cu 2 mm rod.

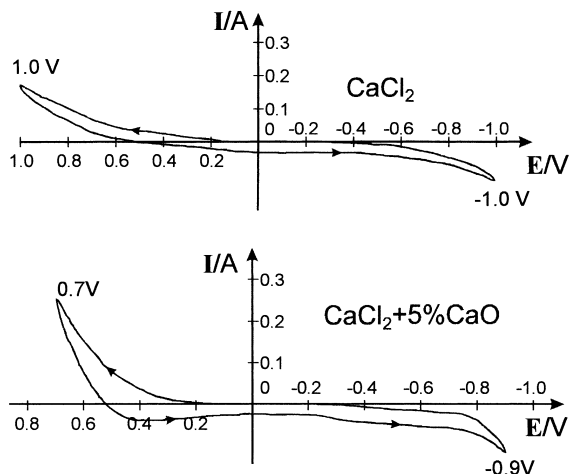


Fig. 3. Cyclic voltammograms on copper in molten CaCl_2 and $\text{CaCl}_2 + 5 \text{ wt } \% \text{ CaO}$ melt at 1073 K, tungsten quasi-reference electrode, scan rate 100 mV s^{-1} .

3. Results and discussion

First, the voltammetric experiments for the calcium chloride melt alone and the calcium chloride melt with oxide additions at 1073 K, with a scan rate of 100 mV s^{-1} , were performed. The voltammograms obtained on the copper working electrode with the use of the tungsten quasi-reference electrode, are presented in Figure 3. The almost flat voltammogram for calcium chloride, indicates the absence of oxy-species in the electrolyte. Some electroactivity as the sweep proceeds, mainly in the anodic direction, and also some during the return sweep in the cathodic direction, can be explained by the fact that calcium chloride which was 'purified' in a simple way, by preheating it only at the temperature of 1000 K, could contain a quantity of oxide in the region 0.1–0.2 M (0.25–0.50 wt %). The voltammograms for melts with additions of calcium oxide revealed a slight increase in current on the anodic branch of the polarization curve, but no change in its cathodic branch.

The voltammograms for copper in $\text{CaCl}_2 + 5 \text{ wt } \% \text{ CaO}$ melts, containing different quantities of calcium carbide, presented in Figure 4(a), (b) and (c) show the direct relation between calcium carbide content and the height of the peak D. The influence of carbide was particularly apparent 900 s after carbide addition in the voltammogram for $\text{CaCl}_2 + 15 \text{ wt } \% \text{ CaC}_2$ (Figure 4(c)). Although the assumption was already made that calcium carbide was soluble, its slow dissolution was confirmed by the results shown in Figure 4(c). The first scan matches exactly the voltammogram shown for $\text{CaCl}_2 + 5\% \text{ CaO} + 5\% \text{ CaC}_2$ in Figure 4(b). The subsequent scans showing larger and larger peaks D, seen clearly even at the lower sensitivity, demonstrate the increased amount of carbide ions in the melt. At the same time the calcium oxidation peak C was the same size, when the peak D was becoming larger and larger as more calcium carbide dissolved.

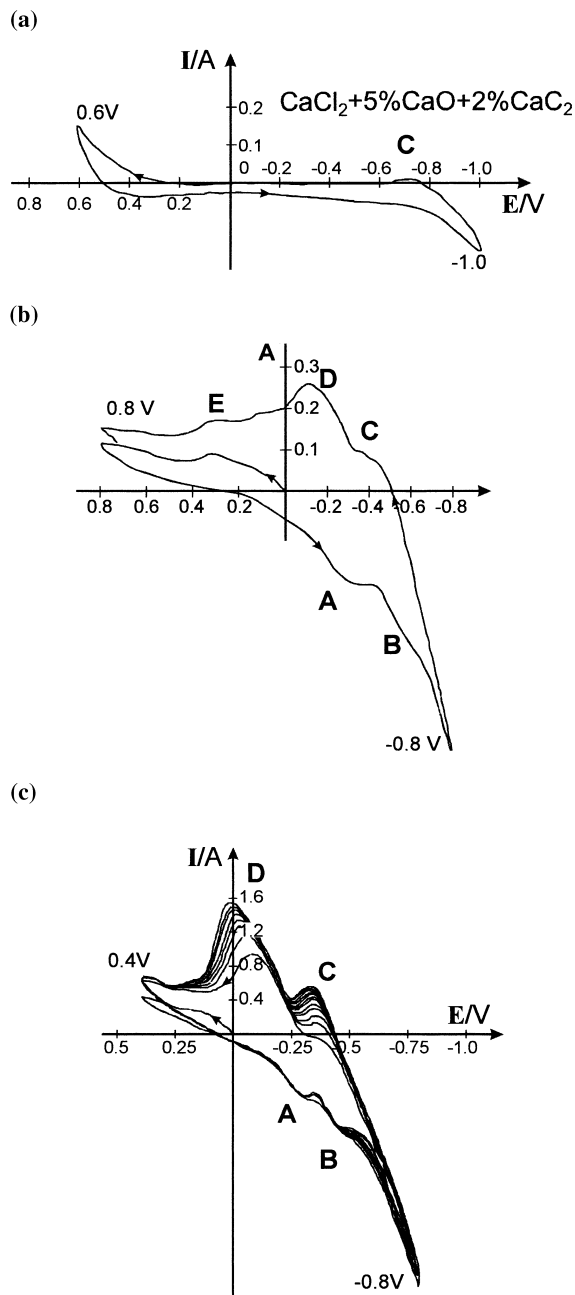


Fig. 4. Voltammograms for copper in $\text{CaCl}_2 + 5 \text{ wt } \% \text{ CaO}$ melt with different amounts of CaC_2 at 1073 K, scan rate 100 mV s^{-1} , 1 h after the addition. (a) 2 wt % CaC_2 , (b) 10 wt % CaC_2 , (c) 15 wt % CaC_2 .

3.1. Reactions in the molten mixture $\text{CaCl}_2 + 5 \text{ wt } \% \text{ CaO} + 5 \text{ wt } \% \text{ CaC}_2$

About 1000 s after the addition of calcium carbide to the calcium chloride melts, peaks C and D appeared on the voltammograms. First, peak C was identified on the reverse, anodic branch of polarization curve (Figure 4(a)), at the potential of about -0.4 V (W_{ref}), then, subsequently peak D, and eventually the remaining peaks A, B and E, were identified.

Based on the direct relationship between the concentration of calcium carbide and the height of the peak D, appearing repetitively on the reverse anodic branch of

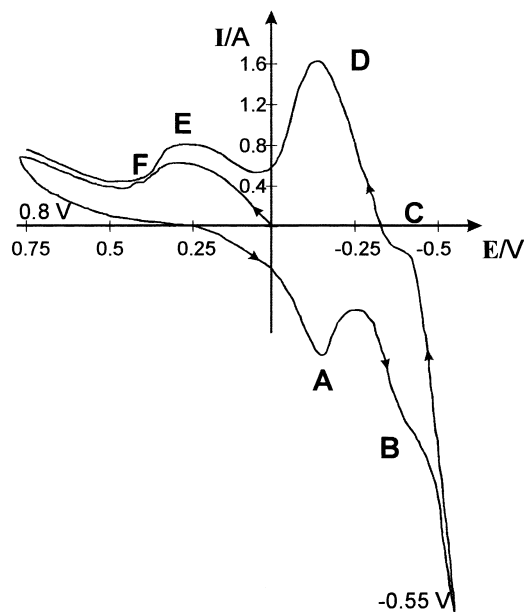


Fig. 5. Voltammogram for copper in $\text{CaCl}_2 + 5 \text{ wt } \% \text{ CaO} + 5 \text{ wt } \% \text{ CaC}_2$, at 1073 K, W_{ref} scan rate 100 mV s^{-1} .

the voltammograms at about -0.15 V , the peak D can be confidently attributed to a process related to the carbide ion C_2^{2-} .

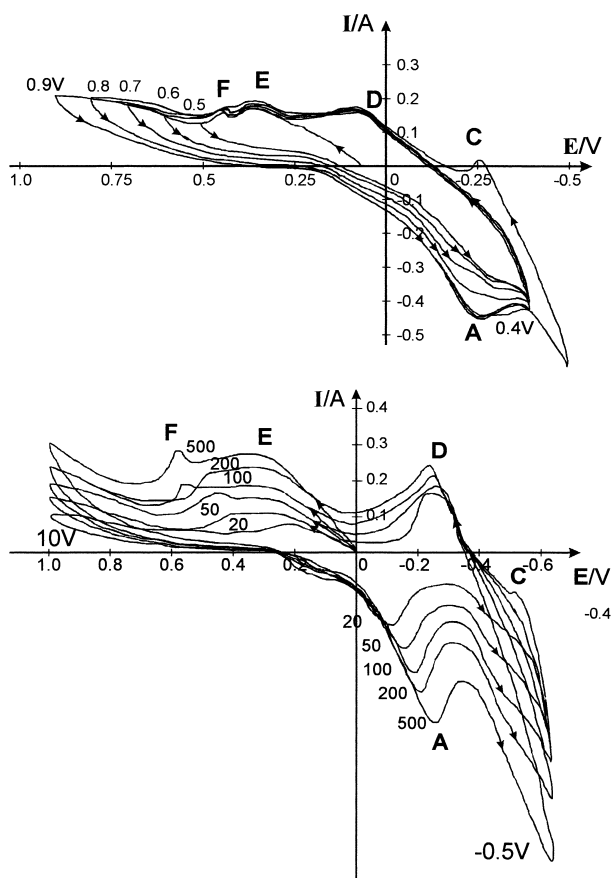


Fig. 6. Voltammograms for copper in $\text{CaCl}_2 + 5 \text{ wt } \% \text{ CaO} + 5 \text{ wt } \% \text{ CaC}_2$, reactions E, F, A, B, C, D at different scan rates and 'potential window'.

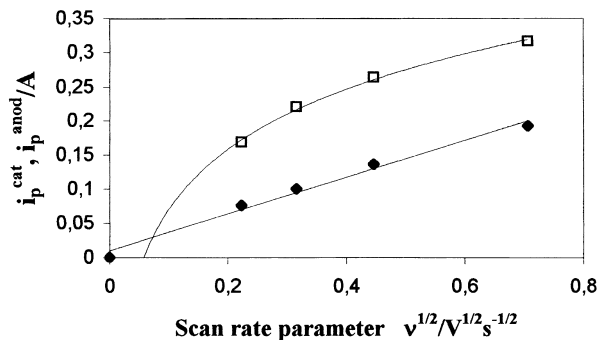


Fig. 7. Dependence of i_p^a and i_p^c on scan rate parameter value $v^{1/2}$. Results of calculations on cyclic voltammetry responses (\blacklozenge) for reaction E (anodic) and (\square) for reaction A (cathodic) on copper is calcium carbide melt at 1073 K.

To identify the reactions corresponding to the peaks A, B and E, systematic voltammetric investigations were undertaken for the selected electrolyte $\text{CaCl}_2 + 5 \text{ wt } \% \text{ CaO} + 5 \text{ wt } \% \text{ CaC}_2$. The voltammograms obtained on copper in this melt are shown in Figures 5–7.

Figure 5 presents the whole set of reactions obtained in the potential range from 0.8 to -0.55 V (W_{ref}), in every case starting from 0 V. Arrows in this figure indicate that the peaks appear on the voltammogram in the following order: E, F, A, B and C, D.

An analysis of the results revealed that peaks B and C can be attributed to the reduction of the calcium ion on the copper electrode and calcium dissolution in the melt, respectively. The cathodic limiting currents always decayed rapidly, after exhibiting a B peak or rather B shoulder, corresponding to calcium reduction. This, in most cases, indicates the decomposition of electrolyte and/or dissolution of electrode. The anodic calcium peak C was revealed during the reverse sweep only when the cathodic potential, lower than -0.6 V vs QRE, was held for a long enough time and the appropriate number of coulombs passed to reduce calcium on copper (Figure 6(a) and (b)). However, focusing on the peak D, the formation of too much calcium on copper was not desirable.

Therefore, the deposition of calcium metal on copper and its dissolution may be attributed to the following waves:

for B



for C



Figure 6, showing the cyclic voltammograms recorded within a different 'potential window' and at different scan rates, clearly indicates the relation between peaks A, E and F. Peak A, which appeared on the voltammogram only when the anodic potential exceeded about $+0.5 \text{ V}$ (W_{ref}), was apparently sensitive to scan rate (Figure 6(b)). The increase in scan rate moved the peak

Table 2. The results of calculations on the cyclic voltammetric responses for reactions A and E in the calcium carbide solution $\text{CaCl}_2 + 5 \text{ wt } \% \text{ CaO} + 5 \text{ wt } \% \text{ CaC}_2$

Scan rate, v $/\text{V s}^{-1}$	$v^{1/2}$ $/\text{V}^{1/2} \text{ s}^{-1/2}$	i_p^a $/\text{A}$	$i_p^a/v^{1/2}$ $/\text{A V}^{-1/2} \text{ s}^{1/2}$	i_p^c $/\text{A}$	$i_p^c/v^{1/2}$ $/\text{A V}^{-1/2} \text{ s}^{1/2}$	i_p^c/i_p^a	E_p^c $/\text{V}$	E_p^c $/\text{V}$	$E_p^c - E_p^a$ $/\text{V}$
0.050	0.223	0.076	0.340	0.168	0.53	0.52	0.214	0.8	0.42
0.00	0.16	0.00	0.16	0.20	0.96	0.54	0.35	-0.61	0.96
0.00	0.47	0.36	0.04	0.64	0.90	0.15	0.64	-0.86	0.50
0.00	0.07	0.92	0.71	0.16	0.46	0.07	0.00	-0.18	0.18

A towards more cathodic potentials, whereas the peak E did not shift with scan rate. Two peaks E and A, which are clearly related to each other, seem to correspond respectively to the oxidation and the reduction of copper.

The results of data analysis for peaks A and B, performed according to an algorithm applied to the reversible cyclic voltammetric response [22, 23] are listed in Table 2.

The differences between the peak potentials, $E_p^c - E_p^a$ (0.40–0.20 V), that is, between the peaks for the oxidation reaction E and the reduction reaction A, were larger than expected for a reversible one-electron process. The dependencies of the values i_p^a and i_p^c on the scan rate parameter $v^{1/2}$ are presented in Figure 7. For the process E, a straight line was obtained with the intercept at the origin, which supports diffusion as the rate controlling process in this case. The ratio i_p^a/i_p^c approached unity when the scan rate was increased. According to [22] this could indicate the presence of a quasi-reversible charge transfer step followed by a nonreversible chemical reaction. To calculate the number of electrons involved in the process, Nicholson and Shain's theory for the charge transfer model [24] was applied to the data. This gave the following number of electrons for the investigated processes E and A: that is $n = 1.4 \pm 0.2$ and $n = 2.2 \pm 0.2$, respectively.

Taking into account the calculated numbers of electrons and the presence of the small peak F at scan rates higher than 0.20 V s^{-1} , the following interpretation of the reactions A and E is the most likely. This is based on remarks by Deutscher and Woods [25] concerning a two-stage copper oxidation process, leading to the formation of Cu^+ and Cu^{2+} and on the information reported by Haufler [26] concerning a thin outer CuO layer above an interior layer consisting of Cu_2O , which is favourably formed by the fast diffusion of copper ions through vacancies in the Cu_2O lattice. In view of the above arguments, the peak F appearing on the voltammograms at the highest scan rates (500 mV s^{-1}), proves the two stage oxidation of copper and its diffusional limitations. Thus, for the investigated reactions A, E and F the following scheme was eventually proposed:

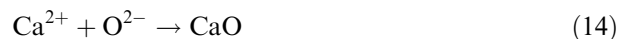
for E



for F



for A



The results obtained indicated that reaction D on the reverse anodic branch was a nonreversible, two-electron process ($\Delta E_p = 0.106 \text{ V}$, $n = 1.88 \pm 0.2$), with a constant ratio $i_p/v^{1/2} = 6.0 \pm 0.3$.

D



A careful examination of reaction D in the potential range from +0.2 to -0.4 V (Fig. 8) revealed the small peak D', appearing repeatedly on voltammograms at the higher sensitivities. Its presence was attributed to the formation of copper carbide [27], which is unstable according to Fromm and Gebhardt [28].

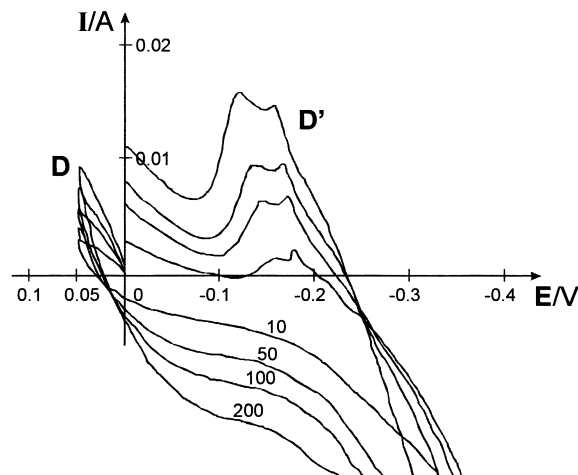
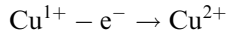
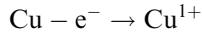


Fig. 8. Voltammogram for reactions D and D' at different scan rates in the range from 0.05 to -0.4 V (W_{ref}) potential range.

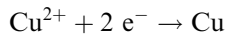
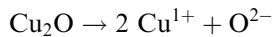
4. Conclusions

The following reactions are likely on solid copper at a temperature of 1073 K, in a melt consisting of $\text{CaCl}_2 + 5 \text{ wt } \% \text{ CaO} + 5 \text{ wt } \% \text{ CaC}_2$, when using a graphite counter electrode vs a tungsten quasi-reference electrode:

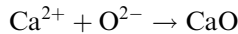
at +0.4 V, the two-stage oxidation of copper



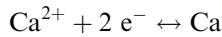
at -0.15 V, the reduction of copper



followed by the chemical reaction

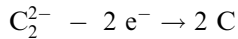


below about -0.45 V, the reversible deposition of calcium

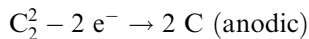
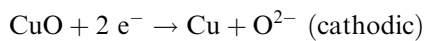


at -0.2 V, the formation of copper carbides CuC_2

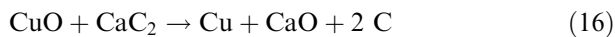
at -0.15 V, the nonreversible oxidation of carbide ion



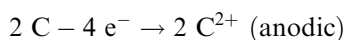
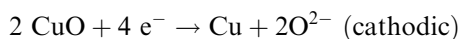
In addition, it can be postulated, that at -0.15 V (W_{ref}), two sets of reactions, appropriately located on the opposite branches of the voltammogram, are possible. These correspond to the oxidation of the carbide ion on the anodic branch and to the reduction of copper oxide on the cathodic branch. They are:



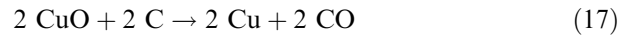
Thus,



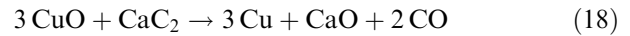
and



Thus,



Adding Reactions 16 and 17, gives:



corresponding to the general reaction (Reaction 1), which confirms the refining ability of carbide in this system, through the electrochemical oxidation of the carbide ion.

References

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