The Electrochemical Reduction of Chromium Sesquioxide in Molten Calcium Chloride under Cathodic Potential Control

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Electrochemical polarization and reduction experiments are reported which were performed with a three-terminal cell and a molten salt electrolyte consisting of calcium chloride with additions of calcium oxide. Employing a metal cathode, a graphite anode and a pseudo-reference electrode also made from graphite, polarization measurements were carried out with the aim to validate the performance of the pseudo-reference electrode and to assess the stability of the electrolyte. Using a chromium sesquioxide cathode in conjunction with a graphite anode and a graphite pseudo-reference electrode, electrochemical reduction experiments were conducted under potentiostatic control. The key results are: a graphite pseudo-reference electrode has been shown to be appropriate in the present type of molten salt electrochemical experiments that take place on a time scale of many hours; the conversion of chromium oxide into chromium metal has been accomplished under cathodic potential control and in the absence of calcium metal deposition; a significant amount of calcium oxide in the calcium chloride has been found necessary to preclude anodic chlorine formation throughout the entire experiment; a considerable overpotential has been identified at the anode.

Key words: Electrochemical Reduction; Calcium Chloride; Chromium Sesquioxide; Chromium; Graphite; Reference Electrode; Anode Overpotential.

1. Introduction

It has been known for several years that it is feasible to convert metal oxides directly into the corresponding parent metals and alloys by way of electrochemical reduction in a molten salt electrolyte [1 – 3]. In this technique, henceforth termed electro-deoxidation, the oxide to be processed is made the cathode, graphite or any other carbon-based material serves as the anode, and an electrolyte is employed that enables the transport of oxide ions from the cathode to the anode. Typically, nominally pure calcium chloride or a mixture of calcium chloride with other chlorides is chosen. During the process, a direct voltage is applied that is sufficiently high to effect decomposition of the metal oxide at the cathode, but low enough to avoid continuous decomposition of the electrolyte. It has been demonstrated that a number of metals and semi-metals may be prepared in this way, with titanium [4 – 12], niobium [13 – 15], chromium [16, 17], silicon [18 – 21], and uranium [22] having thus far received most attention.

Typical electro-deoxidation experiments are performed with two-terminal cells and applied voltages of the order of 3 V. These voltages are below the thermodynamic decomposition potential of calcium chloride which is at approximately 3.2 V at 900 °C, and so continuous electrolysis of the major constituent of the electrolyte is avoided. However, a quantity of calcium oxide is inevitably present as a minor electrolyte constituent, since otherwise no transfer of oxide ions across the cell could take place. The decomposition potential of molten calcium oxide at unit activity is at approximately 2.6 V at 900 °C with respect to the formation of calcium metal and oxygen, but is only at around 1.3 to 1.4 V in the case that calcium metal and carbon monoxide or carbon dioxide are generated, as is expected when using a carbon-based anode. Numbers increase by 116 mV per decade of activity when the calcium oxide is dilute. Under typical experimental conditions, the total voltage applied clearly exceeds the calcium oxide decomposition potential, although it is difficult to quantify for a two-terminal cell, which

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fraction of the applied voltage is effective in the actual reduction and which fraction is lost because of ohmic resistances in the various cell components and polarization phenomena at the two current-carrying electrodes. Therefore, it is impossible to analyse how large the effective voltage was in previous experiments, or to predict how large the total applied voltage should preferably be in future experiments. The decomposition of the dissolved calcium oxide has to be regarded as undesirable because it creates electronically conductive and chemically reducing species. This entails a decrease of current efficiency and renders a clear distinction between electrochemical and chemical reduction problematic.

Improved process control, with the aim of enabling the desired metal oxide decomposition reaction at the cathode whilst avoiding calcium deposition from the electrolyte, may be accomplished through the utilization of a reference electrode. In some of the existing studies, attempts of incorporating reference electrodes into the molten salt electrochemical cells have already been reported. In cyclic voltammetric and short-term chronoamperometric studies, that is, experiments taking place on the timescale of minutes, pseudo-reference electrodes based on materials like titanium, platinum, molybdenum, tungsten, steel or graphite [2, 4, 5, 7, 8, 17, 18, 21] were used. In work on the reduction of silicon dioxide, the well-known silver/silver chloride reference electrode was employed. In one case, the reference system was contained in a thin Pyrex glass tube and used in reduction experiments for no longer than 2 h [18]. In another case, the reference system was located inside a thin quartz tube, and it was observed that signal instability due to erosion occurred during prolonged service [23]. Finally, the silver/silver chloride system was applied in a porous mullite tube, but again only in short-term reduction experiments [19, 20]. In an investigation on uranium oxide reduction it was recognized that the calcium/lead system was likewise not stable over long time periods [22].

In the case of cryolite melts, it is common knowledge that simple reference electrodes based on graphite may be utilized [cf. 24]. By flushing graphite with gaseous carbon oxides, thermodynamically defined reference electrodes of the type $C,CO(g)$; $C,CO_2(g)$ or $C,CO(g),CO_2(g)$ are formed. It has also been shown that, in oxide-containing cryolite melts, a stable electrode potential is created even if no flushing with carbon oxides is carried out, and it is believed that under these conditions a pseudo-reference electrode of the type $C|O^{2-}(l)$ is formed [24]. It was furthermore observed that the electrode potentials of the thermodynamically defined and the pseudo-electrodes were rather similar, with the latter expectedly being dependent on the oxide content of the electrolyte.

It has been the objective of the present study to ascertain the applicability of a graphite-based pseudo-reference electrode in a molten salt electrolyte consisting of calcium chloride and calcium oxide, and this has been done through polarization and electro-deoxidation experiments using a three-terminal cell. Polarization measurements have been performed with a titanium or steel cathode, a graphite anode and a graphite pseudo-reference electrode, aiming to assess the reliability of the pseudo-reference and to identify the potential of calcium deposition. In electro-deoxidation experiments, a chromium sesquioxide cathode has been employed, again together with a graphite anode and a graphite pseudo-reference electrode. Chromium oxide was selected because, firstly, there are no additional phases on the constitutional diagram in between the oxide and the metal [25] which should allow for a rather simple reaction path and, secondly, the feasibility of relatively rapid and current-efficient chromium oxide reduction in an empirically optimized two-terminal cell has already been reported [16, 17]. Calcium chloride with significant additions of calcium oxide has been utilized as the electrolyte. This ensures that the calcium oxide activity is set at a known value, whereas in previous studies no attempt of controlling this quantity was undertaken. A particular target has been to demonstrate that cathodic oxide to metal conversion may be attained under conditions that preclude calcium deposition, so as to realize a clear separation from chemical reduction throughout the entire experiment.

2. Experimental

Chromium sesquioxide, Cr_2O_3, precursors were prepared from a commercially available powder of purity 99+% (metallurgical grade A, Elementis Pigments). Discs were pressed from the as-received powder under a uniaxial pressure of approximately 100 MPa. Sintering was performed at 1400 to 1500 °C in air for 150 min, which provided sufficient mechanical strength for further processing. The resulting compact chromium oxide preforms had approximately the following properties: mass, 2.53 g,

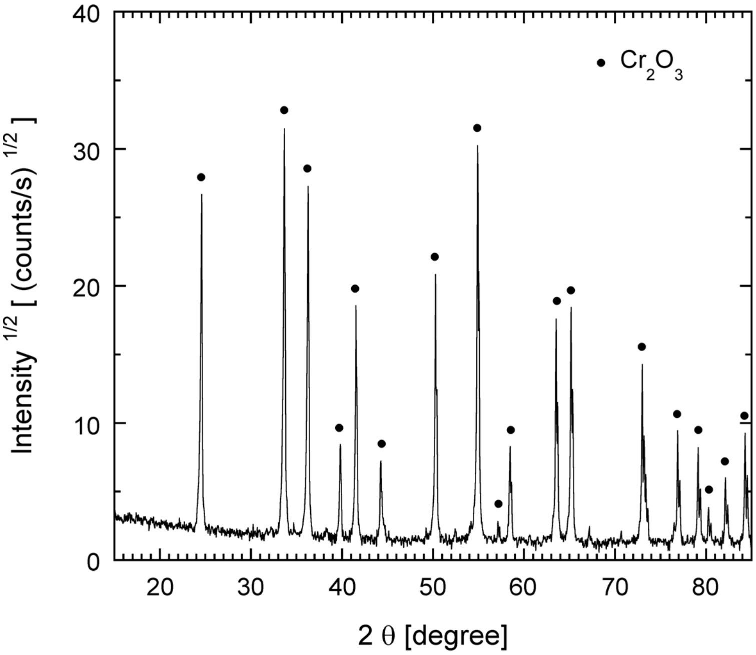


Fig. 1. X-Ray diffractogram of the compact chromium oxide preform after sintering at 1500 °C in air for 2.5 h, showing Cr_2O_3 (•, JCPDS 38-1479). (The small peaks at 67.2° and 70.7° are not present in the experimental reference file, but they are found in most of the simulated reference files and are therefore most probably intrinsic.)

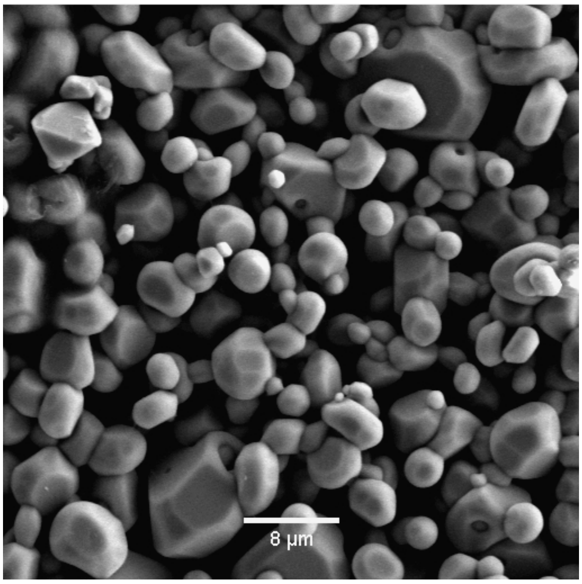


Fig. 2. Scanning electron microscopic image of the Cr_2O_3 preform after sintering at 1400 °C in air for 2.5 h.

corresponding to 0.05 mol of oxygen atoms; diameter, 20 mm; thickness, 3 mm; geometric surface area, 8 cm^2; relative density, 60%; open porosity, 40%. Figure 1 presents an X-ray diffractogram of the precursor material after pressing and sintering, and Fig. 2 shows a scanning electron microscopic image indicating that the particle size in the sintered bodies is in the micrometre range. It may be noted that sintering of chromium oxide in air leads to grain growth but not to shrinkage and densification of the solid body.

The electrochemical experiments were conducted in a cylindrical Inconel® reactor, which was positioned vertically inside a programmable electrical furnace. The reactor was closed with a stainless steel lid, which was equipped with feedthroughs for the lead wires and a thermocouple as well as steel pipes for gas circulation. Argon of conventional purity was dried over self-indicating calcium sulphate and then fed into the reactor.

The molten salt electrolyte consisted of calcium chloride and calcium oxide. Calcium chloride, $CaCl_2$, was obtained from dehydrating calcium chloride dihydrate, $CaCl_2 \cdot 2H_2O$, of nominal purity 99+% (C/1500/65, Fisher Scientific, UK) by gradually increasing the temperature to around 200 °C under vacuum. Acid-base titration confirmed that the oxide content of the so treated calcium chloride was always below 0.1 mol%. Calcium oxide, CaO, was prepared by thermally decomposing calcium carbonate, $CaCO_3$, of purity 99+% (239216, Aldrich) at 1000 °C in air. 218 g of dehydrated calcium chloride and 2.3 g of calcium oxide were filled into an alumina crucible so as to provide an electrolyte containing 98.0 mol% of calcium chloride and 2.0 mol% of calcium oxide. The mixture

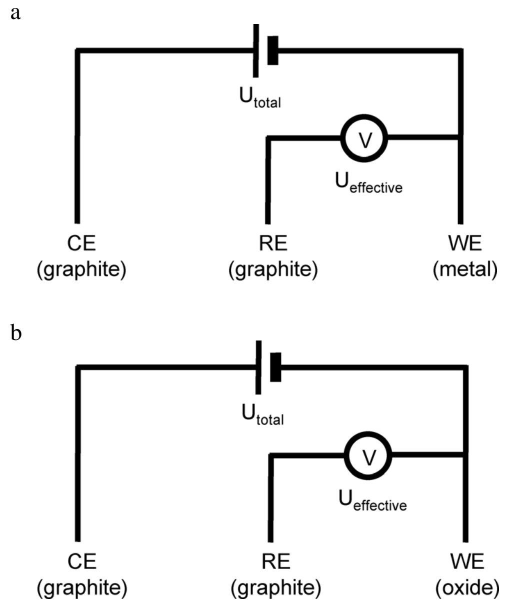


Fig. 3. Schematic drawings of the three-terminal electrochemical cells employed; (a) in polarization experiments using a metal cathode; (b) in electro-deoxidation experiments using an oxide cathode.

was heated under an atmosphere of dried argon and at a ramp rate of 2 °C/min to the operating temperature of 900 °C.

The applicability of the graphite pseudo-reference electrode was assessed through polarization experiments in a three-terminal electrochemical cell. A metal sheet, made of titanium or stainless steel and with a surface area exposed to the salt of around 8 cm^2, was employed as the cathode, and graphite rods of diameters between 6.5 and 10.0 mm (EC4, Tokai Carbon) were used as the anode and as the pseudo-reference electrode. Figure 3a shows a schematic of the electrode configuration. The electrodes were arranged such that the distance between any two electrodes was around 4 cm. Electrical contact to the electrodes was made by means of a nickel wire of 2 mm in diameter which rendered the *IR* drop in the current-carrying leads very small. The electrodes were connected to a computer-controlled potentiostat (Electrochemical Interface SI 1287, Solartron). Each polarization experiment was commenced by applying to the titanium or steel electrode a potential of −0.5 V versus the graphite pseudo-reference electrode. This potential was chosen because it permits electrolysis of water and/or conversion of calcium hydroxide into calcium oxide but avoids decomposition of calcium oxide. The potential of −0.5 V was imposed for at least 12 h, whereafter a small and time-independent background current was always established. The potential was then made more negative by increments of 25 to 100 mV, with the dwell time at each potential step ranging from 1 to 6 h. During each segment the current was recorded as a function of time. The procedure was continued until a dramatic current increase was observed. Several experiments were carried out under nominally identical conditions.

The electro-deoxidation of chromium sesquioxide under a controlled cathode potential was performed in a three-terminal electrochemical cell. A chromium oxide disc was made the cathode, while graphite rods were again used as the anode and as the pseudo-reference electrode. Figure 3b shows a schematic. A thin molybdenum wire was wound around the oxide disc in order to provide mechanical support during processing. As before, the distance between the electrodes was around 4 cm, and a nickel wire was used as the current lead. The reduction experiments were conducted in two stages. First, a voltage ramp was applied in which the potential of the chromium oxide electrode versus the graphite pseudo-reference electrode was gradually shifted to the cathodic target value. Second, the target potential was kept constant for an additional period of time. Typically, the voltage ramp was −300 or −150 mV/h, the target potential was −1.0 V against the graphite pseudo-reference, and the dwell time at the target potential was at least 14 h. During the entire experiment the current was recorded as a function of time. In some cases, the potential difference between the graphite anode and the graphite pseudo-reference electrode was monitored by means of a battery-powered voltmeter. More than 20 reduction experiments were carried out. In addition, a number of partially reduced chromium oxide samples were prepared by early termination of the reduction process.

After each experiment, the furnace was allowed to cool while the sample was left in the salt with the voltage remaining applied. Solidified salt was then removed by rinsing with tap water. The retrieved sample was washed with distilled water, semi-concentrated acetic acid, and again distilled water, each step extending over at least 12 h and involving the application of a mild vacuum of around 20 mbar. Finally, the sample was dried in vacuum at room temperature.

X-Ray diffraction analysis (PW 1710, Philips) was utilized in order to determine the phase composition of the fully and partially reduced chromium oxide

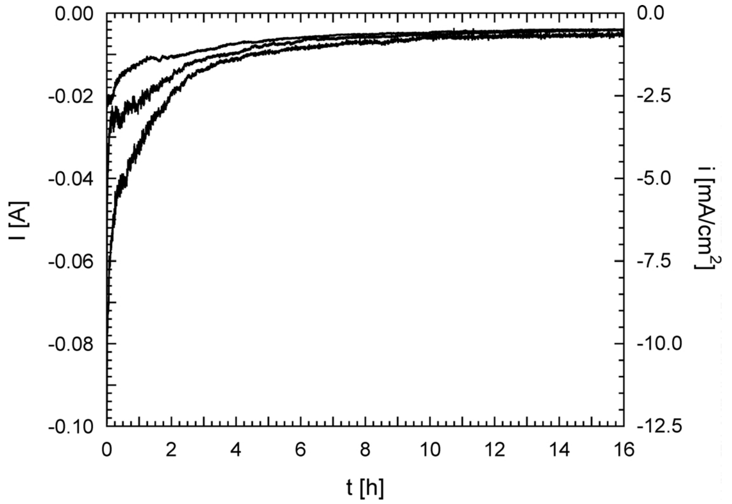


Fig. 4. Current (and current density) versus time curves obtained during polarization experiments at a working electrode potential of −0.5 V versus the graphite pseudo-reference (pre-electrolysis). Electrolyte, calcium chloride with 2 mol% calcium oxide; cathode, steel plate (geometric surface area 8 cm^2); anode, graphite; reference, graphite; temperature, 900 °C; atmosphere, dried argon.

samples. Scanning electron microscopy and energy-dispersive X-ray analysis (JSM-5800LV, JEOL) were employed to investigate the microstructure and chemical composition. Hot extraction (ONH-2000, Eltra) was used for quantitative determination of the oxygen content in fully reduced samples.

3. Results and Discussion

3.1. Validation of the Graphite Pseudo-Reference Electrode

Polarization experiments were conducted with the electrochemical cell represented in Fig. 3a, i. e., by utilizing a virtually oxygen-free inert cathode. Figure 4 shows three representative current versus time curves, which were obtained when applying to the working electrode a potential of −0.5 V versus the graphite pseudo-reference electrode. A significant current was observed at the beginning of each experiment, whereafter the current decayed over several hours until a time-independent background level was established. It is reasonable to assume that the current flow during the initial stage of an experiment is associated with typical pre-electrolysis reactions like the elimination of water or the conversion of calcium hydroxide into calcium oxide [10]. The charge passed during the first few hours was commonly below 1000 C, when disregarding the contribution from the time-independent background current, so the amount of additionally formed calcium oxide was low. In order to determine the content of calcium oxide in the calcium chloride after pre-electrolysis, melt samples were taken and subjected to acid-base titration. It was found that the calcium oxide content was always between 2.0 and 2.2 mol%. This shows that the effective calcium oxide content of the electrolyte subsequent to melting and pre-electrolysing was indeed only marginally increased beyond the nominal level. This is in agreement with previous findings [10]. The final current in the present type of experiment was usually around 5 to 10 mA, corresponding to a cathodic current density of the order of 1 mA/cm^2. It is believed that this current originates from electronic conduction through the electrolyte. To some extent the current may also be due to the removal of trace amounts of oxygen from the metallic cathodes or the presence of redox-active impurities in the electrolyte.

Upon incrementally changing the potential of the working electrode to values around −0.9 V versus the graphite pseudo-reference electrode, the current remained at low levels, and the cathodic current density was always below 15 mA/cm^2. Figure 5 presents current versus time curves that were obtained at potentials between −1.0 V and −1.5 V. Under these conditions, the current increased dramatically and, at around −1.4 V and beyond, the cathodic current density reached and exceeded values of 100 mA/cm^2. The currents and current densities measured were averaged, when necessary disregarding the early stage of a segment where the current was sometimes unsteady, and plotted in Fig. 6 as a function of the potential. The lower abscissa shows the applied potential with respect to the graphite pseudo-reference, while the upper abscissa gives the applied potential with respect to the Ca/Ca^{2+} standard, as discussed in greater detail below. The graph indicates that there is good consistency

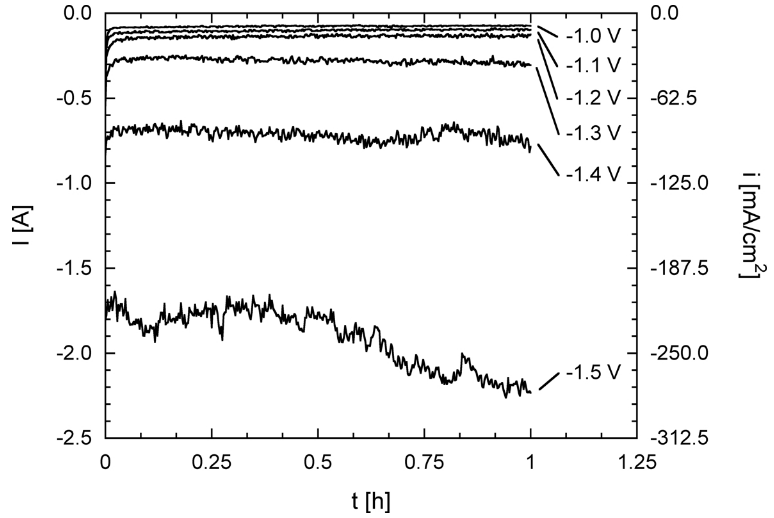


Fig. 5. Current (and current density) versus time curves obtained during polarization experiments at working electrode potentials between −1.0 and −1.5 V versus the graphite pseudo-reference. Electrolyte, calcium chloride with 2 mol% calcium oxide; cathode, steel plate (geometric surface area 8 cm^2); anode, graphite; reference, graphite; temperature, 900 °C; atmosphere, dried argon.

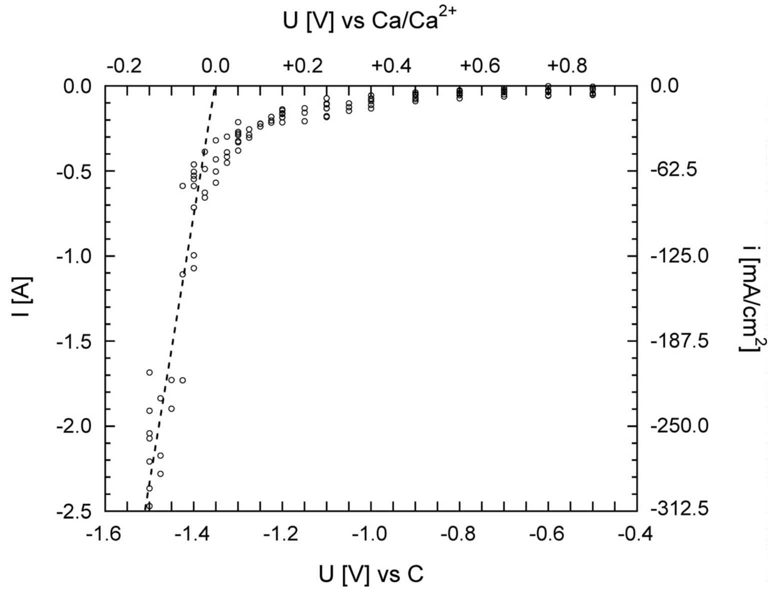


Fig. 6. Current (and current density) versus potential curves showing averaged currents (and current densities) as a function of the working electrode potential versus the graphite pseudo-reference (lower abscissa) and the Ca/Ca^{2+} standard (upper abscissa). Electrolyte, calcium chloride with 2 mol% calcium oxide; cathode, steel plate (geometric surface area 8 cm^2); anode, graphite; reference, graphite; temperature, 900 °C; atmosphere, dried argon.

between the numerous individual experiments. The occurrence of high currents at increasingly negative potentials is an intrinsic property of the electrolyte and is based on the solubility of calcium metal in molten calcium chloride [26]. As a consequence, species containing calcium in the oxidation states one and zero may exist in the melt at less than unit calcium activities [27, 28], and their concentration rises significantly as the calcium deposition potential is approached. This renders it straightforward to attribute the marked current increase to the enhanced formation of reduced and dissolved calcium-based electronic charge carriers in the melt.

In Fig. 6, the reversible potential of calcium deposition has been identified through linear extrapolation to the abscissa of the steep part of the current versus potential curve. The graph illustrates that, for an electrolyte composition of 98 mol% calcium chloride and 2 mol% calcium oxide and a temperature of 900 °C, the pseudo-potential of the graphite reference electrode is approximately 1.35 V anodic of the reversible potential of calcium deposition. Using available thermodynamic data [29], it is possible to give a more quantitative account of the relevant potentials. In the following, E and E^O are the reduction potential and the standard reduction potential, respectively; R, T and

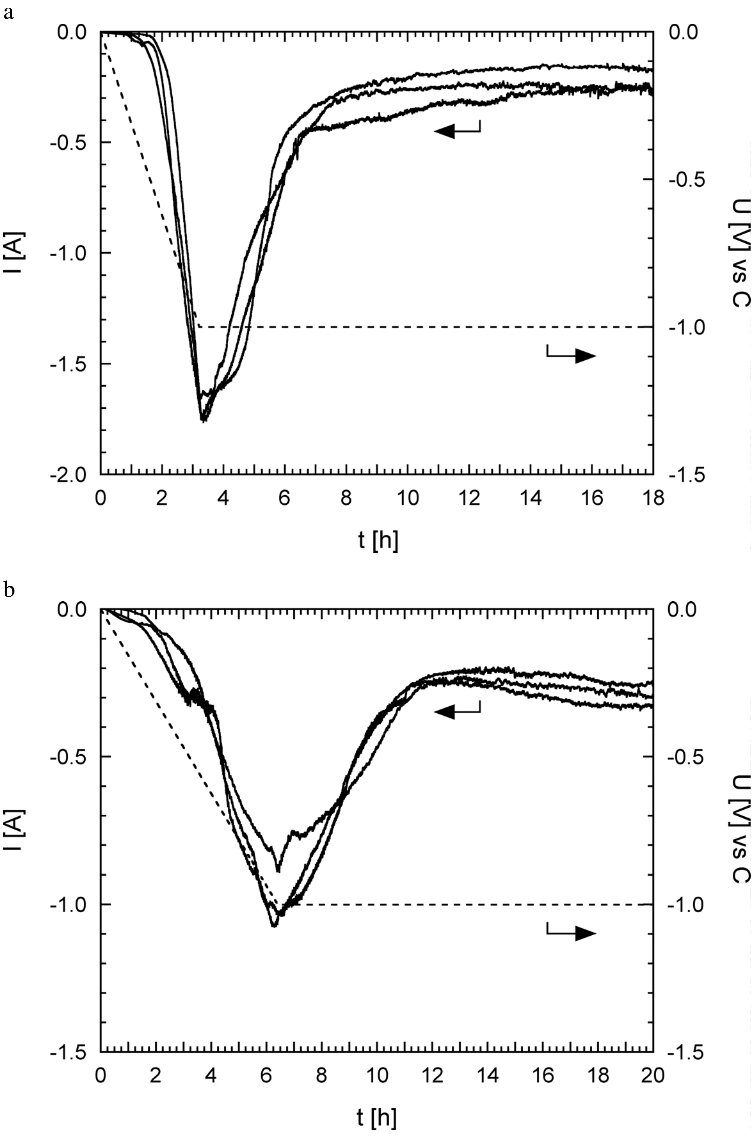


Fig. 7. Current versus time curves obtained during electro-deoxidation experiments, with the potential of the working electrode ramped to, and maintained at, −1.0 V versus the graphite pseudo-reference; (a) ramp rate −300 mV/h; (b) ramp rate −150 mV/h. Electrolyte, calcium chloride with 2 mol% calcium oxide; cathode, Cr_2O_3 disc (geometric surface area 8 cm^2); anode, graphite; reference, graphite; temperature, 900 °C; atmosphere, dried argon.

F are the universal gas constant, the absolute temperature and the Faraday constant, respectively, and a is the activity of the species indicated. The standard states for both solids and liquids, gases, and ions are chosen as the pure compound, the atmospheric pressure, and the unit mole fraction of the relevant ionic sublattice, respectively [10]. The reduction potential of the Ca/Ca^{2+} redox couple is given by the expression

$$\begin{aligned}&Ca^{2+} + 2e^- = Ca,\\ &E = E^{O} - \frac{RT}{2F}\ln\frac{a_{Ca}}{a_{Ca^{2+}}} \quad \text{with } E^{O}_{1173\,K} = 0\text{ mV}.\end{aligned} \tag{1}$$

As pure calcium metal and the unit mole fraction of calcium ions are the standard states, the potential of this electrode is at $E = 0$ mV. The reduction potential of the C/CO couple is given as

$$\begin{aligned}&CO + 2e^- = C + O^{2-},\\ &E = E^{O} - \frac{RT}{2F}\ln\frac{a_{O^{2-}}}{a_{CO}} \quad \text{with } E^{O}_{1173\,K} = +1287\text{ mV}.\end{aligned} \tag{2}$$

For a calcium oxide mole fraction of 0.02, a carbon monoxide pressure of 1 atm, and a temperature of 900 °C, the potential of this electrode amounts to $E = +1664$ mV with respect to the Ca/Ca^{2+} standard.

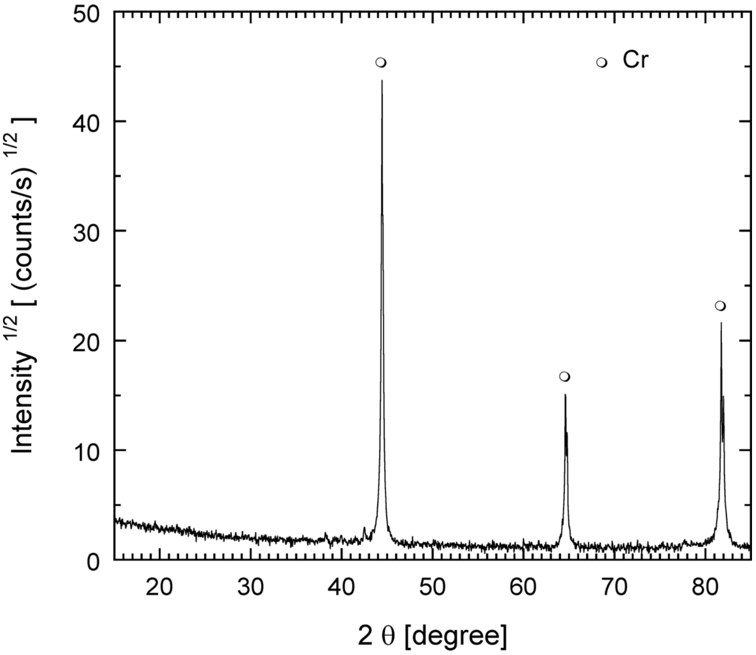


Fig. 8. X-Ray diffractogram of a sample retrieved at the end of an electro-deoxidation experiment, showing Cr (○, JCPDS 06-0694).

Note that the reference state for oxide ions refers to pure supercooled calcium oxide, and that the corresponding activity coefficient of $\gamma = 0.029$ has been used, as follows from $RT \ln \gamma = -70831$ kJ/mol $+ 30.99\,T$ kJ/(mol K) [30]. The analysis shows that the potential of the graphite pseudo-reference electrode is, for the given experimental conditions, by approximately 300 mV more cathodic than that of the corresponding reversible electrode involving a carbon monoxide gas phase at atmospheric pressure.

In conclusion, the results of the present section have proven that the pseudo-potential, which is established at the contact between graphite and a molten mixture of calcium chloride and calcium oxide, is characterized by satisfactory time-stability and reproducibility, and is linked in a defined manner to the reversible potentials of common redox couples. These findings, combined with the excellent thermal and chemical long-term stability of graphite in molten salts as well as its ease of application, suggest the incorporation of a graphite pseudo-reference electrode in laboratory-scale electro-deoxidation experiments.

3.2. Cathode Reactions in the Electro-Deoxidation of Chromium Sesquioxide

Electro-deoxidation experiments were conducted with the electrochemical cell represented in Fig. 3b, and employing a chromium sesquioxide, Cr_2O_3, cathode. Figures 7a and b display the current versus time curves that were recorded during various experiments, which involved ramping the potential of the working electrode to, and then maintaining it at, -1.0 V versus the graphite pseudo-reference electrode. The diagrams show that the current is small for small applied potentials but increases significantly at potentials in the range of -0.3 to -0.6 V. Around the target potential the current peaks and remains at a high level for a few minutes. Then the current decreases gradually and reaches a relatively stable background level. Figures 7a and b illustrate that there is good agreement between the different current traces over a total processing time of many hours. This confirms the suitability of the reference electrode used. Notably, comparison of Figs. 7a and b with Fig. 6 demonstrates that there is substantial current flow at potentials far below that of calcium deposition. This proves the occurrence of electrochemical reactions that do not require the presence of deposited calcium metal.

In total, more than 20 chromium sesquioxide samples were processed under the conditions described above, and all the reduced samples were light grey in colour and had a matt metallic appearance throughout their entire volumes. The samples were rather friable, but it was always possible to recover fragments of sufficient size to enable straightforward examina-

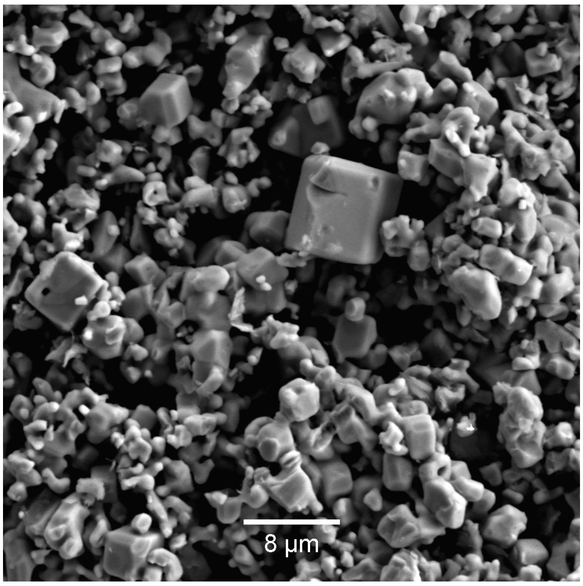


Fig. 9. Scanning electron microscopic image of Cr metal prepared by electro-deoxidation.

tion. In each case, X-ray diffraction analysis proved the presence of phase-pure chromium metal. Figure 8 presents a typical X-ray diffractogram. Scanning electron microscopy revealed a porous and rather heterogeneous microstructure with particle diameters ranging from submicron to around 10 μm. Particles were lightly sintered together and their shapes varied between spherical and cubic, which agrees with previous findings [16]. A characteristic micrograph is shown in Figure 9. Energy-dispersive X-ray analysis confirmed the overwhelming presence of chromium. No, or only minute, calcium and chlorine signals were detected, and no significant amounts of other impurities were identified. The quantitative determination of the oxygen content by means of the hot extraction technique consistently yielded values between 750 and 1500 ppm by mass, provided the rigorous recovery and drying practice outlined above was carried out. When applying procedures that involve temperatures in excess of room temperature, oxygen contents increased, typically to numbers in the range of 1500 to 5000 ppm. Overall, the present results have demonstrated unequivocally that the conversion of chromium oxide into chromium metal is feasible under conditions that preclude the deposition of calcium metal from the molten salt electrolyte onto the cathode.

In order to gain an insight into the kinetic pathway of electro-deoxidation of chromium sesquioxide to chromium metal, a number of partially reduced samples were prepared. This was done by terminating the reduction process at, or around, the current peaks that are visible in Figs. 7a and b. The retrieved, washed and dried samples were subjected to various investigations, and a number of important observations were made.

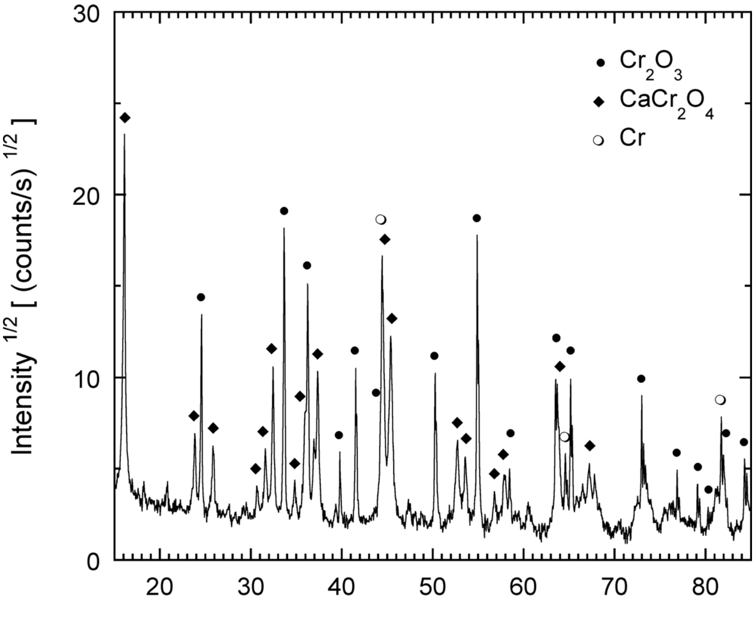
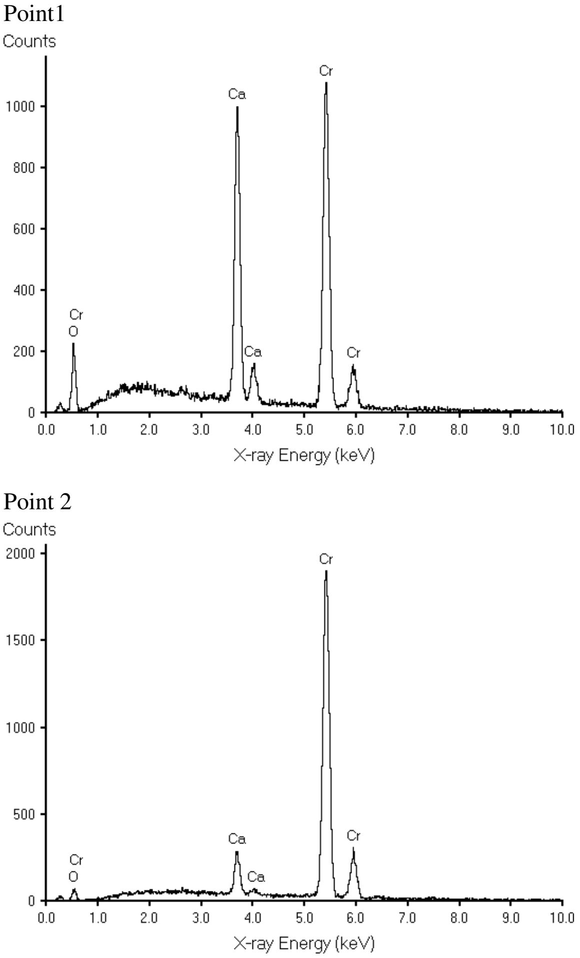


Fig. 10. X-Ray diffractogram of a sample retrieved after passing about 50% of the charge theoretically needed to achieve complete conversion, showing Cr_2O_3 (●, JCPDS 38-1479), $CaCr_2O_4$ (◆, JCPDS 48-0203) and Cr (○, JCPDS 06-0694).



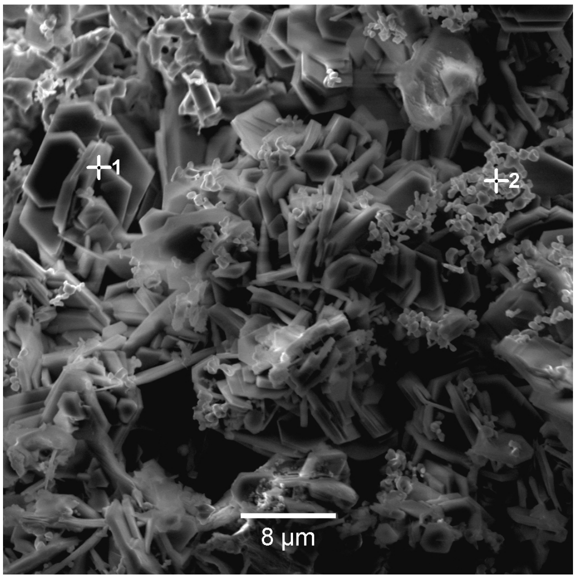


Fig. 11. Scanning electron microscopic image of a sample retrieved after passing about 50% of the charge theoretically needed to achieve complete conversion, showing a domain of Cr and $CaCr_2O_4$ as well as energy-dispersive X-ray spectra from points 1 and 2.

Samples quenched near the current peak had gained in mass. X-ray diffraction analysis revealed that only three phases are present to a significant extent in the course of an electro-deoxidation experiment, these being chromium sesquioxide, Cr_2O_3, calcium chromite, $CaCr_2O_4$, and chromium metal, Cr, which clarifies that chromium occurs in the oxidation states three and zero only. With time, the amount of Cr_2O_3 falls and the amount of Cr rises, while $CaCr_2O_4$ only exists temporarily. A typical X-ray diffractogram obtained from a partially reduced sample is presented in Figure 10. Electron microscopic investigation of fracture surfaces has shown further that partially reduced samples consist of numerous domains with different degrees of reduction. There are regions that contain only Cr_2O_3 and have the same appearance as the precursor. Other regions are characterized by the presence of $CaCr_2O_4$ and Cr metal. Figure 11 shows a typical micrograph of such an area with platelets of $CaCr_2O_4$ and fine spheres of Cr metal. Overall, the amount of visible Cr metal appears smaller than that deemed from the amount of charge passed and the intensity of Cr in the X-ray diffraction trace, but it is possible that some of the Cr metal was engulfed by the $CaCr_2O_4$ particles. A similar observation had indeed been made in the reduction of titanium dioxide, where titanium suboxide particles were fully enclosed by calcium titanate particles [11]. It is important to note that Cr_2O_3 and Cr metal were never found to co-exist in direct contact. As expected, the degree of reduction was larger at the edge of a partially reduced sample than in the centre. However, a three-phase boundary that moves uniformly from the outside toward the inside of a sample was not seen in this set of experiments.

The key findings concerning the determination of the kinetic pathway of electro-deoxidation of chromium sesquioxide in calcium chloride are, firstly, the fact that Cr metal is not formed directly from Cr_2O_3 and, secondly, the temporary presence of substantial amounts of $CaCr_2O_4$ in partially reduced samples. Control experiments have shown that the chemical reaction between calcium oxide dissolved in calcium chloride and a porous chromium sesquioxide sample at 900 °C is sluggish. After 10 h of exposure only a very thin film had formed around the surface of the Cr_2O_3 sample while there was no or very little $CaCr_2O_4$ inside the sample and the overall mass change was too small to be determined reliably. It may therefore be deduced that the $CaCr_2O_4$ present in partially reduced samples is generated electrochemically. Analogous observations had been made in the reduction of titanium dioxide [10, 11], where the initial formation of the various titanium suboxides, TiO_{2-x}, $0 < x \leq 1$, and calcium titanate, $CaTiO_3$, occurs in a combined reaction. Calcium is inserted into the cathode, with calcium ions stemming from the electrolyte and electrons being injected at the negative terminal, oxygen is redistributed, and the calcium incorporated causes a mass gain. The calcium-containing compounds are then reduced in subsequent reactions, which involve the release of both oxide ions and calcium ions. Based on the experimental evidence obtained in the present study, a similar reaction scheme is proposed for the reduction of chromium sesquioxide, and this comprises the following two reaction steps:

$$4\,Cr_2O_3 + 3\,Ca^{2+} + 6\,e^- = 2\,Cr + 3\,CaCr_2O_4, \quad E^{O}_{1173\,K} = +1560\ \text{mV}, \tag{3a}$$

$$CaCr_2O_4 + 6\,e^- = 2\,Cr + Ca^{2+} + 4\,O^{2-}, \quad E^{O}_{1173\,K} = +778\ \text{mV}. \tag{3b}$$

The standard electrode potentials quoted for the above reaction steps were calculated from thermodynamic data [29] for unit activities and a temperature of 900 °C and refer to the Ca/Ca^{2+} standard. It is evident that the formation of chromium metal under the given experimental conditions is in full accordance with thermodynamic expectations. Combining the above two reaction steps yields the anticipated overall reaction

$$Cr_2O_3 + 6\,e^- = 2\,Cr + 3\,O^{2-}. \tag{4}$$

To conclude, it may be stated that the preferred cathodic reaction sequence in the electro-deoxidation of chromium sesquioxide encompasses, firstly, the incorporation of calcium into the cathode, involving the concomitant generation of reduced chromium metal and an unreduced calcium-containing compound, and, secondly, the reduction of this compound, involving the simultaneous release of oxide ions and calcium ions into the electrolyte. Reaction (4) expresses the overall process but does not reflect the kinetic pathway. Moreover, it has been clarified that calcium exists exclusively in the oxidation state two throughout the entire electro-deoxidation process. Although calcium ions play an active role in the reduction process and are temporarily found in the cathode, they are never discharged, and calcium metal is never formed. Therefore, the reduction proceeds in an entirely electrochemical manner and no calciothermic reaction step is required.

3.3. Electrolyte-Related Issues

In a foregoing investigation into the electrochemical reduction of titanium dioxide [10], experiments were performed with a conventional two-terminal cell, total applied voltages between 2.5 and 2.9 V, and a molten salt electrolyte that consisted of calcium chloride with little dissolved calcium oxide, typically not more than 0.1 to 0.3 mol%. Cathodic current densities of up to 250 mA/cm^2 were encountered during the initial stage of the process, and it was realized that these were mainly supported through the decomposition of a quantity of calcium chloride. The presence of chlorine in the offgas was proven analytically, and very little anode consumption was found to occur in the early phase of the process. In contrast, no chlorine has been detected in the present study, and carbon consumption commenced immediately after starting an experiment. This means that current densities of the order of 200 mA/cm^2, as recorded during some of the current peaks, were sustained by oxide ions alone, and that the anode reaction was the formation of carbon oxides.

The examination of partially reduced chromium sesquioxide samples has revealed that a calcium-containing compound temporarily forms part of the cathode. It has been reasoned that this compound is generated through the electrochemical insertion of calcium into the cathode according to reaction (3a), and that the corresponding anode reaction is the release of carbon oxides. Therefore, while compound formation is taking place, the concentration of calcium oxide in the molten salt electrolyte is lowered. During decomposition of the compound according to reaction (3b), both oxide ions and calcium ions are released back into the electrolyte. Consequently, while compound decomposition is ongoing, the calcium oxide concentration of the electrolyte is raised again. Obviously, the composition of the electrolyte after reduction will be identical to that before reduction. Temporary variations of the calcium oxide concentration in the electrolyte may have two implications. Firstly, the potential of the graphite pseudo-reference electrode is altered because of its dependence on the oxide ion activity of the melt. Secondly, the transport properties of the electrolyte may be affected, as the maximum oxide ion transfer rate depends on the oxide ion concentration in the melt. However, these effects remain minor as long as the change in calcium oxide concentration is small compared with the initial concentration[1], and they vanish once the compound decomposition is completed.

A further issue regarding the dissolved calcium oxide in the electrolyte relates to its reaction with carbon dioxide, which is expected to be one of the anode products. It is known that carbon dioxide possesses significant solubility in calcium oxide-containing calcium chloride, and that this is caused by the formation of dissolved carbonate ions [31, 32], which may be described by the redox equilibrium

$$CO_3^{2-} + 4e^- = C + 3O^{2-}. \qquad (5)$$

During the formation of carbonate ions at the anode, the above reaction proceeds from right to left and entails a decrease in the concentration of oxide ions in the electrolyte. Toward the end of reduction, the release of oxide ions from the cathode decreases gradually, and the same is true for the oxidation of carbon at the anode. In the absence of a significant thermodynamic carbon dioxide pressure, the carbonate ions start decomposing and the initial calcium oxide concentration is progressively restored. In line with the argumentation in the preceding paragraph, it is clear that the change of the calcium oxide concentration in the electrolyte has an impact on the performance of the electrochemical cell but, as long as the deviation is reversible, the effect is temporary. Overall, carbonate formation and decomposition are difficult to quantify[2], and it is therefore an important empirical finding that the sustained high oxide ion current density and the absence of chlorine evolution throughout each experiment prove that the calcium oxide concentration remains at a significant level at all times. A noteworthy observation in this context is that at the end of an experiment, some finely divided carbonaceous powder loosely surrounds the processed sample and floats on the surface of the salt melt, particularly in the vicinity of the cathode assembly. It is intimately mixed with the salt and can be removed readily through rinsing with water during sample retrieval. The occurrence of the carbonaceous powder is thought to be a consequence of the above redox reaction. At the anode, carbonate ions are formed through the oxidation of carbon and, at the cathode, elemental carbon is released through the reduction of carbonate ions. Hence, reverse reactions take place at both electrodes whereby carbon is transferred electrochemically from the anode to the cathode.

A particular complication of the calcium chloride/calcium oxide system arises from the significant solubility of calcium metal in calcium chloride. The latter amounts to approximately 3.7 mol% at 900 °C [26]. Under the given experimental conditions, the formation of calcium at unit activity was found to occur at a potential of approximately -1.35 V versus the graphite pseudo-reference electrode. The most cathodic value applied during oxide reduction was at -1 V versus the graphite pseudo-reference, corresponding to $+0.35$ V versus the Ca/Ca^{2+} standard. Under these conditions, the equilibrium calcium activity is at $9.8 \cdot 10^{-4}$ which relates to a mole fraction of $3.6 \cdot 10^{-5}$. It is acknowledged that such an electrolyte composition constitutes a chemically reducing medium, but it is also evident that the concentration of dissolved calcium metal is insufficient to account for the comparatively large current densities and high rates of reduction observed in Figs. 7a and b. Consequently, chemical reduction remains negligible as long as the cathode is kept at potentials significantly more positive than that of calcium deposition. However, if

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[1] In the present set of experiments, the initial amounts of Cr_2O_3 in the cathode and of CaO in the electrolyte are 0.0167 and 0.04 mol, respectively. In view of (3a), 0.0125 mol CaO would be removed from the electrolyte if the entire cathode were transformed into a homogeneous mixture of Cr and $CaCr_2O_4$. This would temporarily lower the CaO content from 2.0 mol% to approximately 1.38 mol%. In practice, the amount of CaO involved in compound formation at any time is yet smaller for it has been noticed that the transformation of the cathode does not occur in an entirely uniform manner.

[2] There are several reasons as to why it is virtually impossible to assess quantitatively the amount of CaO involved in the formation of carbonate. The magnitude of the carbon dioxide partial pressure is location-dependent, with the pressure being higher at the anode than in the argon-filled space above the melt; the carbon dioxide partial pressure is time-dependent, as the release rate of carbon dioxide varies throughout the different stages of reduction; it is not known how rapid the kinetic response of the electrolyte is to changes of the carbon dioxide pressure.

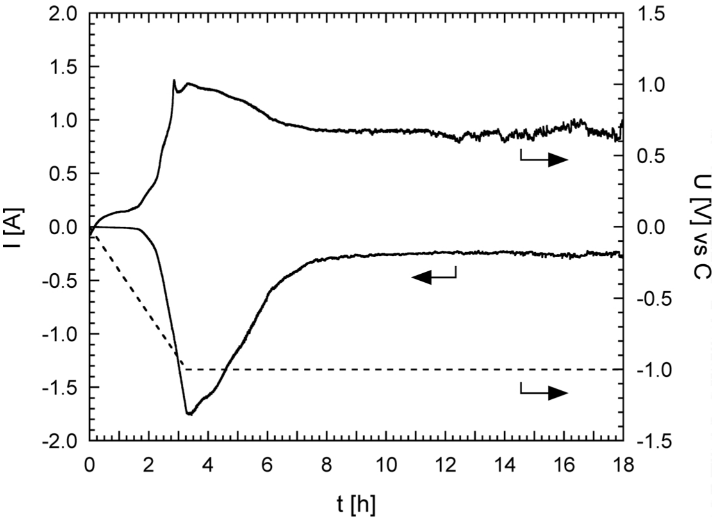

Fig. 12. Anode overpotential versus time curve obtained during an electro-deoxidation experiment. The upper curve is the overpotential, the lower two curves have been taken from Fig. 7a; for details see Figure 7a.

the potential of the cathode approaches or exceeds that of calcium deposition, the enhanced electronic conduction of the electrolyte will gradually lower efficiency of the reduction process, and the presence of dissolved calcium may interfere with a plain electrochemical reduction pathway. It has already been elaborated that these features are of relevance in the final stages of titanium dioxide reduction [10].

In summary, the results of the present section have demonstrated that the concentration of calcium oxide in the calcium chloride-based electrolyte is an important parameter in the electro-deoxidation process. The calcium oxide concentration needs to be sufficiently high in order to allow for a high oxide ion transfer rate through the electrolyte and preclude chlorine formation at the anode at large current densities. However, in the course of the reduction, some of the calcium oxide is temporarily removed from the electrolyte through the formation of a calcium-containing compound in the cathode and the generation of carbonate ions dissolved in the electrolyte. Both effects are transient, so the original calcium oxide concentration is gradually re-established as reduction approaches completion. Therefore, changes of the pseudo-reference potential are temporary and long-term process control is possible. The latter is unambiguously proven by the good consistency and reproducibility of the curves in Figs. 7a and b.

3.4. The Anode Overpotential

It is common practice in electro-deoxidation experiments to utilize two-terminal electrochemical cells, including an oxide-based cathode and a carbon-based anode, with total applied voltages of the order of 3 V [2, 3, 5, 6, 9 – 17, 21]. More specifically, it has been shown that the reduction of chromium sesquioxide remains incomplete if the total voltage is restricted to values at or below 2.5 V at 950 °C [17]. On the contrary, the present study has confirmed that a voltage of as low as 1 V between the oxide electrode and an unpolarized graphite electrode suffices to convert chromium sesquioxide into chromium metal. This indicates that substantial voltage losses exist in two-terminal cells, which render the effective voltage significantly lower than the total applied voltage, and it may be assumed that these occur primarily at the carbon-based anode.

In order to assess the performance of the anode, the potential difference between the graphite anode and the graphite pseudo-reference electrode was monitored throughout the course of some of the electro-deoxidation experiments. In this way, the potential of the anodically polarized graphite electrode was compared against that of an unpolarized graphite electrode, i. e., the anode overpotential was identified. A typical result is presented in Figure 12. During the first stage of the process, the increasing current leads to a rise of the anode overpotential, and it is seen that both quantities exhibit a similar time-dependence. At the current peak, the anode overpotential is at approximately 1 V, that is, the potential difference between cathode and reference electrode and the overpotential at the anode are of the same order of magnitude. When the current decreases, the anode overpotential falls too, but the decline of overpotential is somewhat delayed. Interestingly, even when the oxide ion current becomes negligible and only the background current persists, the anode overpotential remains at values of several hundred millivolts, while complete depolarization only occurs after terminating polarization.

The discharge of oxide ions from a calcium chloride/calcium oxide electrolyte at a carbon-based material has been the subject of a number of studies in the literature [33 – 35]. It has been elucidated that this process takes place in several steps. Initially, oxide ions are released through the dissociation of complexes that are thought to exist in the melt [36], whereupon they form an adsorbate of the type C_xO at the carbon surface. This step is accompanied by the transfer of two electrons per oxide ion. The adsorbate then reacts further with oxide ions from the melt and carbon dioxide is released as the main gaseous product. This step involves another two-electron transfer. The reaction sequence may be described as follows:

$$O^{2-}(\text{complex}) = O^{2-}(\text{dissociated}), \tag{6a}$$

$$O^{2-}(\text{dissociated}) + xC = C_xO(\text{adsorbed}) + 2e^-, \tag{6b}$$

$$\begin{aligned} &O^{2-}(\text{dissociated}) + C_xO(\text{adsorbed}) \\ &= CO_2(g) + (x-1)C + 2e^-. \end{aligned} \tag{6c}$$

The studies cited have demonstrated that the above reaction sequence is accompanied by significant kinetic limitations, and this is the explanation of the appreciable polarization losses at the anode found in the present case. Moreover, the formation of well-defined and stable adsorbates consisting of oxygen and carbon is likely to be the reason for the adequate performance of the graphite-based pseudo-reference electrode.

The occurrence of a substantial anode overpotential readily accounts for the fact that the total applied voltage in two-terminal cells needs to be significantly in excess of the voltage that is thermodynamically required to achieve oxide reduction. Being a kinetic quantity, the anode overpotential is expected to depend on a number of cell parameters, like current density, electrode geometry, and reactivity of the carbon-based material used, and may also change with time and vary between individual experiments. While these factors may be eliminated in a three-terminal cell, they have a considerable impact on reproducibility in conventional two-terminal cells.

The existence of a large anode overpotential is of fundamental importance to the understanding of electrochemically induced oxide reduction processes. The present study has clarified that the direct and complete conversion of chromium sesquioxide into chromium metal in molten calcium chloride may be achieved in an electrochemical manner, that is, through the expulsion of oxide ions under the influence of a cathodic potential. In contrast, other researchers have expressed the belief that the actual reduction step is of a purely chemical nature [37, 38], and a reaction sequence has been proposed that comprises the steps of deposition of calcium metal onto the surface of the cathode, chemical reduction of the cathode through the calcium metal formed, and dissolution of the resulting calcium oxide into the electrolyte. These ideas have been supported by the observation that, in the processing of titanium dioxide with a two-terminal cell, a noticeable extent of reduction was only achieved if the total applied voltage was above approximately 1 V [38], and it has been reasoned further that the required calcium metal is generated by in-situ electrolysis of calcium oxide. There is always a small quantity of calcium oxide present in a calcium chloride melt, either because it has been removed incompletely during electrolyte pretreatment or because it is inevitably formed during reduction. However, in the light of the present results, it has to be considered that a two-terminal cell with a carbon-based anode possesses a marked anode overpotential, in addition to other possible voltage losses, and so it is plausible to assume that the effective voltage in the above case was considerably lower than 1 V and probably rather of the order of 0.5 V. Under these conditions, the formation of mixtures of titanium suboxides, TiO_{2-x}, $0 < x \leq 1$, and calcium titanate, $CaTiO_3$, is predicted [10, 11], which is indeed in accordance with the reported findings [38]. Overall, the observation of the onset voltage of metal oxide reduction in a two-terminal cell being close to the thermodynamic decomposition voltage of calcium oxide, is a mere coincidence, caused by neglecting the impact of the anode overpotential, and interpretations based thereupon ought to be revised.

To summarize, the results and argumentation above have revealed that the anodic discharge of oxide ions at a carbon-based anode in a molten calcium chloride-based electrolyte is accompanied by a substantial overpotential. This finding underscores the importance of adequate process control in the given type of experiment, and it uncovers fundamental misapprehensions in other studies.

4. Conclusion

Using a three-terminal cell that contains an inert metal cathode as well as a graphite anode and a graphite pseudo-reference electrode, polarization measurements were performed in order to assess the cathodic stability limit of a calcium chloride/calcium oxide molten salt electrolyte. It was possible to identify the onset of significant electronic conduction in the electrolyte and thus the potential of calcium deposition. By means of a three-terminal cell that involves a chromium sesquioxide cathode in addition to a graphite anode and a graphite pseudo-reference electrode, electro-deoxidation experiments were performed under the conditions of controlled cathode potential. Experiments were carried out such that decomposition of the chromium oxide to chromium metal was enabled, whilst deposition of calcium metal onto the cathode was precluded. The results have unambiguously clarified that calcium deposition is not a requirement in the electro-deoxidation process. It has also been shown that calcium ions play an active role in the reaction, although they never change their oxidation state, and that the calcium oxide content of the electrolyte is subject to time-dependent variations.

The present study has demonstrated that the incorporation of a graphite pseudo-reference electrode into an electro-deoxidation cell may provide improved process control in experiments that are conducted at laboratory scale and extend over a time period of many hours. The particular advantage of this approach consists in the straightforward applicability of graphite in high-temperature cells. It remains to be seen whether the same approach is feasible in scaled-up plants. It has further been revealed that the anodic release of carbon oxides is a highly polarized reaction, which has an adverse effect on process control in conventional two-terminal cells. In future work, the anode reaction and related issues should be examined more intensively.

It is anticipated that the reduction of the oxides of, for instance, iron, nickel, manganese, niobium, tantalum and uranium may be accomplished under conditions similar to those applied in the present study, which is the consequence of the comparatively low thermodynamic stability of these oxides. In contrast, the preparation of metals like titanium, zirconium and hafnium from their relatively stable oxides will require significantly more cathodic potential, and this will inevitably entail increased electronic conduction in the molten salt electrolyte and diminished current efficiency.

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