



Measurement of Counter Electrode Potential during Cyclic Voltammetry and Demonstration on Molten Salt Electrochemical Cells

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Authors' contributions

This work was carried out in collaboration between all authors. Author DSMV designed the study, performed the experimental work and wrote the first draft of the manuscript. Authors NS and KSM helped in analysis of the experimental data and suggested additional experiments to arrive at meaningful conclusions. All the authors managed the literature searches. All the authors read and approved the final manuscript.

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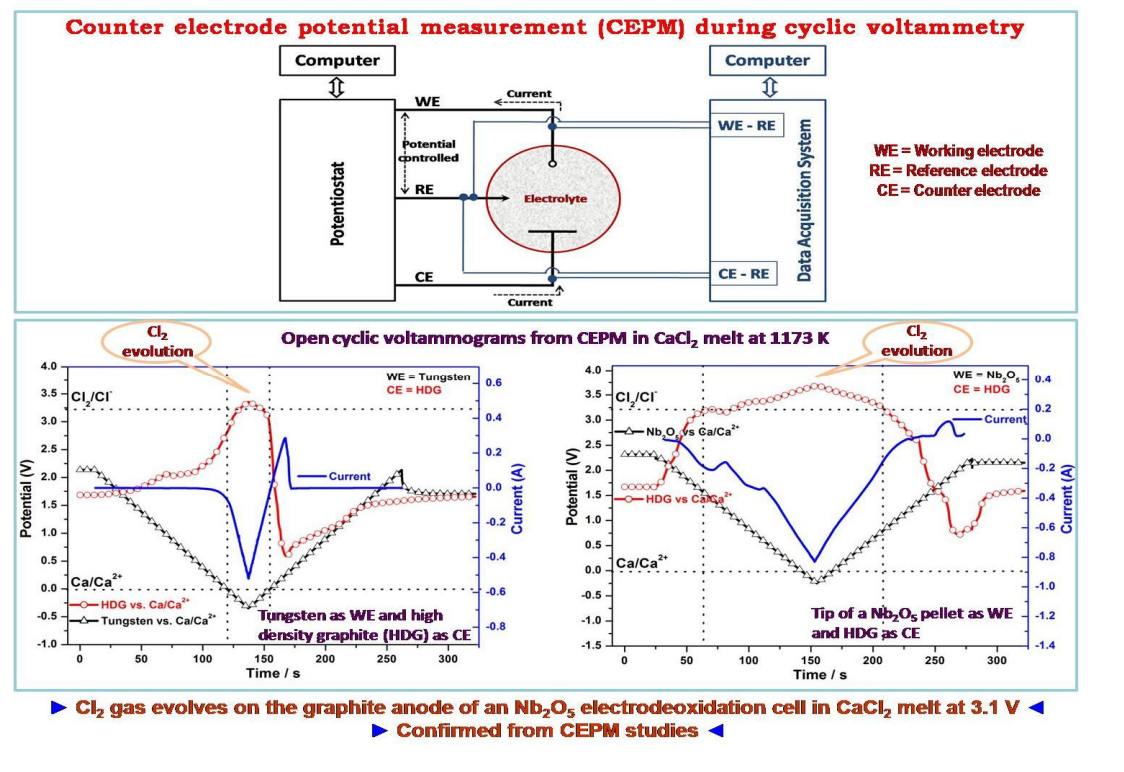
ABSTRACT

In conventional cyclic voltammetry (CV) measurements, the potential of the working electrode (WE) is changed at a fixed scan rate w.r.t a reference electrode and the current response to the potential stimuli recorded. The current-potential data are in turn related to the redox behavior of the electroactive species in the electrolyte on the WE. The contribution of the counter electrode (CE) to the electrical signals has been suppressed by design to avoid its influence on the I-V characteristics of the WE. However, simultaneous measurement of the counter electrode potentials during CV measurements can provide useful qualitative information on the electrochemical process/es occurring at the CE and thus help in the comprehensive assessment of the overall electrochemical process/es under question. This has been demonstrated with tungsten and graphite WEs respectively against graphite and molybdenum CEs in CaCl_{2-x} wt.% CaO melts ($x = 0$ and 1) at 1173 K. The technique has been applied to CV cell with Nb_2O_5 pellet as the WE against graphite

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CE in CaCl_2 melt and the results prove that preliminary information on the electro-deoxidation of the oxide electrode could be achieved by the novel measurements.

Graphical abstract



Keywords: Cyclic voltammetry; Counter electrode potential; Calcium chloride; Nb_2O_5 ; FFC Cambridge process; Electro-deoxidation.

1. INTRODUCTION

Cyclic voltammetry (CV) is a potential-controlled reversal electrochemical technique used extensively in the study of electrode reactions and mechanisms [1]. The CV cell comprises of three electrodes, viz. the working electrode (WE), the counter electrode (CE) and the reference electrode (RE) and the electrolyte solution in contact with the electrodes. In this technique, the working electrode is applied with a cyclic potential varying at a given scan rate w.r.t a reference electrode and the corresponding currents are monitored. In a typical CV cell, the area of the CE is made very high compared to that of the WE so that the current density on the latter becomes very high and that of the former very low. This in turn ensures that the WE remains highly polarized and the CE negligibly polarized so that the electrical responses in the cell circuit can be attributed mainly to the

electrochemical process/es occurring at the WE of the cell. This in other words means that the role of CE in a traditional CV experiment is limited to its use as an electrode to complete the cell circuit with WE, otherwise no information is sought to be obtained from the CE.

Though CV in its rigorous sense is generally used as an analytical technique for study of fundamental electrode processes and mechanism of redox systems, the technique can also be used in a simple manner to obtain both qualitative and quantitative information of electrode processes occurring in an electrochemical cell. For example, the technique can be used to experimentally determine the electrochemical window of ionic melts like CaCl_2 [2], LiCl [3] etc. and hence in the estimation of standard free energy of formation of the salts [2,3]. This information is necessary while carrying out electrolysis experiments in the molten salts.

Further, the absence of any irregular current wave/s between the discharge potentials of the cation and anion of the electrolyte melts gives a clear indication that the melts are free of any significant redox active impurities. Mohandas et al. [4] employed the technique to obtain semi-quantitative information on the anodic intercalation and cathodic de-intercalation of chlorine occurring on graphite in NaAlCl_4 melts at 425 K - 580 K and in turn used the results to study the physical degradation of graphite anodes in the melt and its temperature dependence. The technique was also used to distinguish between the adsorption and intercalation of chlorine occurring on anodically polarized graphite electrode in NaAlCl_4 melts [5]. The CV technique has been used very effectively to obtain qualitative information on different electrode reactions of both the electrodes of molten salt electro-deoxidation cells [2,6-8]. In most of these measurements CV technique was used only in a limited sense, i.e. to apply a cyclic potential to the working electrode and to obtain the corresponding currents, which in turn could be related to the reaction taking place at the working electrode. We have studied the electro-deoxidation behavior of TiO_2 [9-10] and Nb_2O_5 [3] electrodes in CaCl_2 melt with graphite anode and UO_2 electrode in $\text{LiCl-Li}_2\text{O}$ and CaCl_2 -48mol.% NaCl melts with both graphite [11,12] and platinum anodes [2,12]. The CV technique was used extensively in these studies to determine the electrochemical window of the molten salts and also to understand the electrochemical behavior of the oxide working electrode and graphite and/or platinum counter electrodes. During these measurements, it was observed that practically useful information on the electro-deoxidation cells can be obtained by measuring the potential of the counter electrodes, which otherwise is ignored. The counter electrode potential measurement (CEPM) presented in this article is thus a simple extension of the CV technique to derive first hand information on electrode processes occurring at the CE of a CV cell. The technique has been demonstrated with tungsten and graphite WEs against graphite and molybdenum CEs respectively in pre-electrolysed CaCl_2 and CaCl_2 -1wt.% CaO melts at 1173 K. The novel measurements carried out on a CV cell with Nb_2O_5 pellet as the WE against graphite CE in CaCl_2 melt demonstrated its capability to provide qualitative information of the multiple electrode reactions occurring on both cathode and anode of the molten salt electro-deoxidation cell. Such information, gained rather quickly from a single experiment, is helpful in

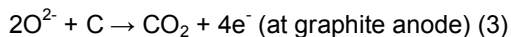
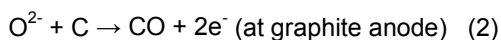
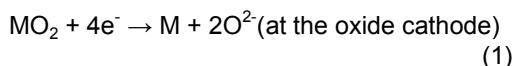
gaining insight into the electro-deoxidation of the oxide electrode and also in the operation of the electro-deoxidation cells. All the demonstration experiments, reported in this study, were carried out with electrode/electrolyte systems whose reactions were well studied and reported before so that the potential-current data of the CV-CEPM measurements could be correlated to the known electrode reactions of each system studied. A rigorous study and analysis of the electrochemical behavior of the WE w.r.t. scan rate is not warranted in this kind of measurements and hence the measurements were carried out at a single scan rate (20 mV/s) only.

1.1 The CEPM Measurement

While recording the cyclic voltammogram of a WE, electrochemical reaction/s corresponding to that occurring at the WE takes place at the CE. The potential of the CE is left free and allowed to float while running a conventional CV. In CV-CEPM, the counter electrode potential w.r.t. reference of a CV cell is simultaneously measured using a high-impedance voltmeter and the measured potentials are related to the electrochemical process/es occurring at the electrode. The half cell reaction/s at the WE (CV) when combined with the corresponding half cell reaction/s at the CE (CEPM) together defines the overall electrochemical process/es taking place in the cell and thus serves as a good source of first-hand information on the net cell reaction/s.

1.2 Application of CV-CEPM Measurement on Molten Salt Electro-deoxidation Cell

Direct electrochemical deoxidation of solid metal oxides to metal in the 'FFC Cambridge process' is an interesting area of development in electrometallurgy and significant R&D work has been reported in this area [13,14]. The electrolytic process is carried out by configuring the oxide electrode, generally prepared as a pellet by powder compaction and sintering, as the cathode against graphite counter electrode in calcium chloride melt at ~ 1173 K. During the process, the oxygen present in the metal oxide is ionized to O^{2-} ions (oxygen ionization) and released to the electrolyte melt. The ions subsequently discharge as CO and/or CO_2 gas at the graphite anode even as the metal oxide electrode converts itself to the corresponding metal. The electrode reactions can be written as



As electro-deoxidation of the oxide cathode takes place, corresponding oxidation reactions occur at the graphite counter electrode so as to maintain the electro-neutrality of the cell. In the absence of O^{2-} , oxidation of Cl^- ions could occur at the electrode as



The measurement of the graphite counter electrode potential enables identification of the anodic reactions of the cell even as the oxide WE is being reduced by the imposed cathodic potential. Also, as discussed later, some more reactions can occur at both the electrodes of an electro-deoxidation cell, thus making the overall electrochemical process of the cell a complex one. Under this condition, a CV experiment carried out in the melt and simultaneous measurement of the counter electrode potential of the cell helps to identify the reactions taking place at both the electrodes from a single experiment and hence in the better understanding of the electrochemical processes occurring in the cell. Some such novel measurements have been demonstrated on typical molten salt cells, the results of which are discussed in this article.

2. EXPERIMENTAL

Anhydrous CaCl_2 was prepared from $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Extra pure, Merck) by vacuum drying of the hydrated salt as described in Ref. [6]. An argon atmosphere glove box with moisture level less than 5 vppm was used in the storage and handling of the dried salts. An alumina crucible (75 mm dia. x 110 mm long) was loaded with the required amount of salt and the crucible was placed inside a stainless steel reactor vessel. Electrodes were introduced into the vessel in a leak-tight manner through the provisions made on the top flange of the vessel and whole reactor assembly was made leak-tight with the help of O-ring seal. The reactor assembly, maintained under continuous flow of high-purity argon gas, was heated to 1173 K using a resistive heating furnace in conjunction with a programmable temperature controller (Shinko, Japan). The

molten salt was pre-electrolysed at 2.8 V for 6 hours to remove moisture and redox active impurities present in it and subsequently allowed to cool overnight. Appropriate quantity of CaO was added to the pre-electrolysed and frozen CaCl_2 salt to obtain CaCl_2 -1 wt.% CaO composition and the mixture was again heated to 1173 K. The melt was allowed to remain overnight at that temperature to aid dissolution of CaO in the CaCl_2 melt. A tungsten wire (1 mm dia.) and the tip of a Nb_2O_5 pellet (20 mm dia., 2.3 mm thick and weighing 2.94 g) were used as the WEs (1 mm length of tungsten in the former case and 4 mm vertical length of the pellet in the latter case were immersed into the melt during study) for cathodic polarization against a high density (HD) graphite rod (10 mm dia., supplied by M/s. Nickunj Group, Mumbai) as the counter electrode (3.6 cm was the immersion length). A molybdenum coil (made from 1 mm dia. Mo wire) was used as the CE during the anodic polarization of the HD graphite rod in the melt. A Ni/NiO system [8] was employed as the reference electrode. Unless otherwise mentioned, CV measurements were carried out at a scan rate of 20 mV/s with the help of a potentiostat (Autolab PGSTAT-30). A data acquisition/switch unit (Agilent 34970A) was used to record the potentials of the WE (vs. the reference) and CE (vs. the reference). The half cell potentials were converted to the Ca/Ca^{2+} potential scale and presented in this paper. The Ca/Ca^{2+} potential of melt was obtained by cyclic voltammetry of W electrode in the CaCl_2 melt. A schematic of the CV-CEPM cell and the electrode/measurement arrangement are shown in Fig. 1.

A cyclic voltammogram is generally represented as a plot of current vs. potential. As the potential also includes time (scan rate, mV/s), the data can be plotted with current as a function of time, which obviously opens up the otherwise closed cyclic voltammogram. For the sake of clarity, the current vs. potential voltammograms shown in this article are called 'Closed Cyclic Voltammograms (CCV) and the current/potential vs. time traces as 'Opened Cyclic Voltammogram (OCV)'. As mentioned previously, in this study, it is only aimed to generate qualitative information on the electrode process occurring in the CV cell and to relate it to the electrochemical cell under study. It is not intended to use the data for conventional analytical purposes, as is usually done with cyclic voltammetry technique.

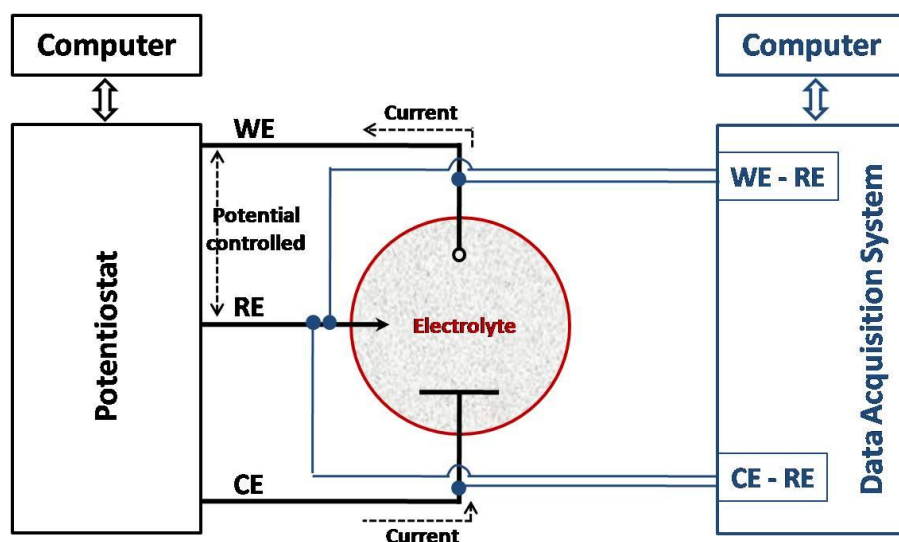
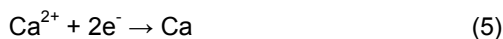


Fig. 1. Schematic of the CV-CEPM cell and the electrode/measurement arrangement (CE = Counter electrode, WE = Working electrode and RE = Reference electrode)

3. RESULTS AND DISCUSSION

3.1 The CV of Tungsten and Graphite Electrodes in CaCl₂ AND CaCl₂ - 1 wt.% CaO

The Closed Cyclic Voltammogram (CCV) of tungsten and graphite working electrodes in the pre-electrolysed calcium chloride melt are given in Fig. 2a and Fig. 2b, respectively. The corresponding Opened Cyclic Voltammograms (OCV) are given in Figs. 2c and 2d, respectively. The straight-line portions of the plots in Fig. 2a and Fig. 2b were extrapolated to zero current to obtain the reversible potentials of the two reactions



and reaction (4) as 0.00 V (vs. Ca/Ca²⁺) and 3.23 V (vs. Ca/Ca²⁺), respectively. Thus the electrochemical window of the calcium chloride melt was determined as 3.23 V. This agrees well with the reversible decomposition potential of CaCl₂ at 1173 K deduced from the Gibbs energy data (CaCl₂ → Ca + Cl₂ (g), Δ_rG^o_{1173K} = 619.625 kJ/mol., E^o_{1173K} = - 3.231 V) [15].

The small currents observed on the respective electrodes before commencement of reaction (4) and (5) and which increase with increase in the applied potential show that some electrochemical reactions other than the two reactions take place on the respective electrodes. The underpotential

current on tungsten electrode is attributable to the following reactions [16].



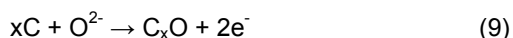
The high solubility of calcium metal in the CaCl₂ melt [17] drives the above reactions. The anodic current at potentials cathodic to the chlorine evolution potential (reaction 5) arises from the anodic adsorption of Cl⁻ on the graphite as per the reaction [18,19]



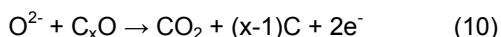
The results of the CV of tungsten electrode (cathodic polarisation) and graphite (anodic polarisation) in CaCl₂ melt containing 1 wt.% CaO at 1173 K are given in the CCVs shown in Fig. 3a and 3b and the corresponding OCVs in Fig. 3c and 3d. When compared to the CVs of the electrodes in pure CaCl₂ melt (Fig. 2a and 2b), the current of the CVs in Fig. 3a and 3b at any potential can be seen to be higher.

The CaO present in the calcium chloride melt forms CaCl₂-CaO complex with the melt [20] and the high cathodic current is related to the reduction of the complex, though the mechanism is not clearly understood. The high cathodic current could also be arising from the cathodic reaction of in-situ generated CO₃²⁻ in the melt as discussed in section 3.3. Oxide ions in the melt

adsorb on the active surface sites of the anodically polarised graphite as per the reaction



and subsequently undergoes the following reaction to produce CO₂ gas



The reactions (9) and (10) adds to make reaction (3). Reaction (3) is thermodynamically favoured than reaction (4) and hence the predominant reaction on graphite anode in CaCl₂-CaO melts is the former one. From thermodynamic data [15], the potential of reaction (3) and (4) are estimated as 1.625 V and 3.231 V vs. Ca/Ca²⁺ at 1173 K. The reaction (3) is associated with significant overvoltage so that the reaction takes place at oxidation potentials significantly higher than that estimated theoretically [8]. This is evident from Fig. 3b too. The lower activity of

CaO in melt (1 wt.% CaO against the saturation solubility of ~12 wt.%) is also a reason for the positive shift in the anodic CO₂ formation potential.

3.2 CV-CEPM IN CaCl₂ Melt Using Tungsten as the WE

Fig. 4 shows the results of CEPM carried out during cathodic polarisation of tungsten against the Ni/NiO reference electrode in CaCl₂ melt. During CV, the potential of the WE was scanned from 0.0 V to -2.5 V and back to 0.0 V. The corresponding potentials of the graphite CE, measured simultaneously with the help of the high-impedance voltmeter, and the corresponding cell currents are also given in the figure. The reversible Ca/Ca²⁺ and Cl⁻/Cl₂ potentials of the CaCl₂ melt determined by the CV measurements (Fig. 2a and 2b) are shown in the figure by dotted lines parallel to x-axis.

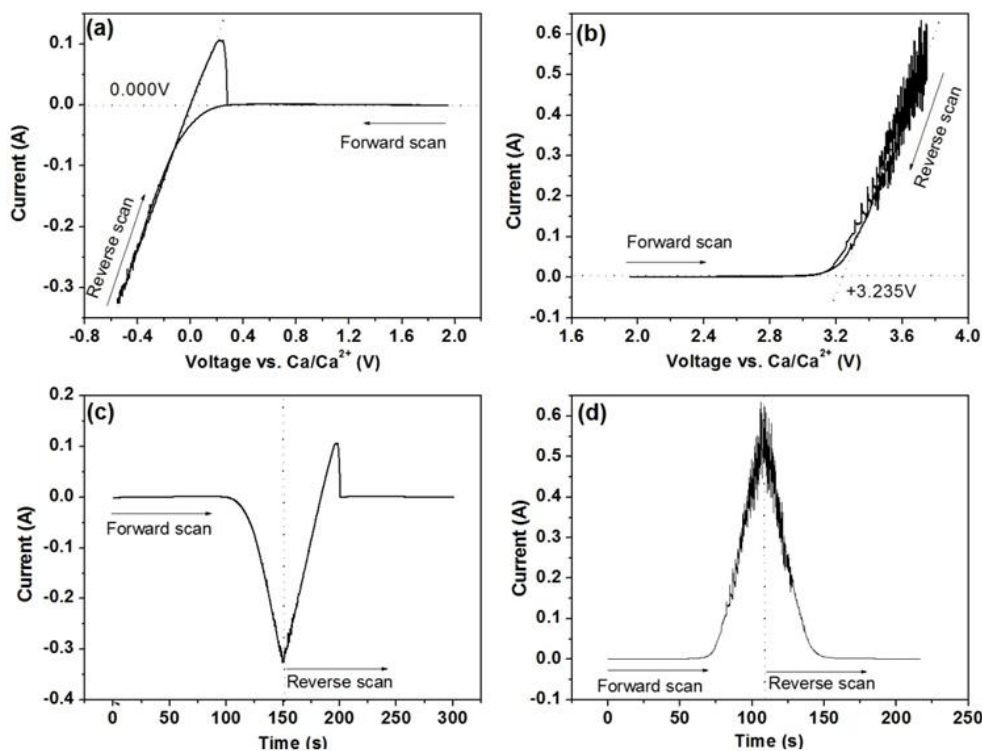


Fig. 2. Closed cyclic voltammograms (CCVs) recorded in CaCl₂ melt at 1173 K on (a) tungsten and (b) graphite working electrodes. (c) and (d) represent the corresponding open cyclic voltammograms (OCVs)

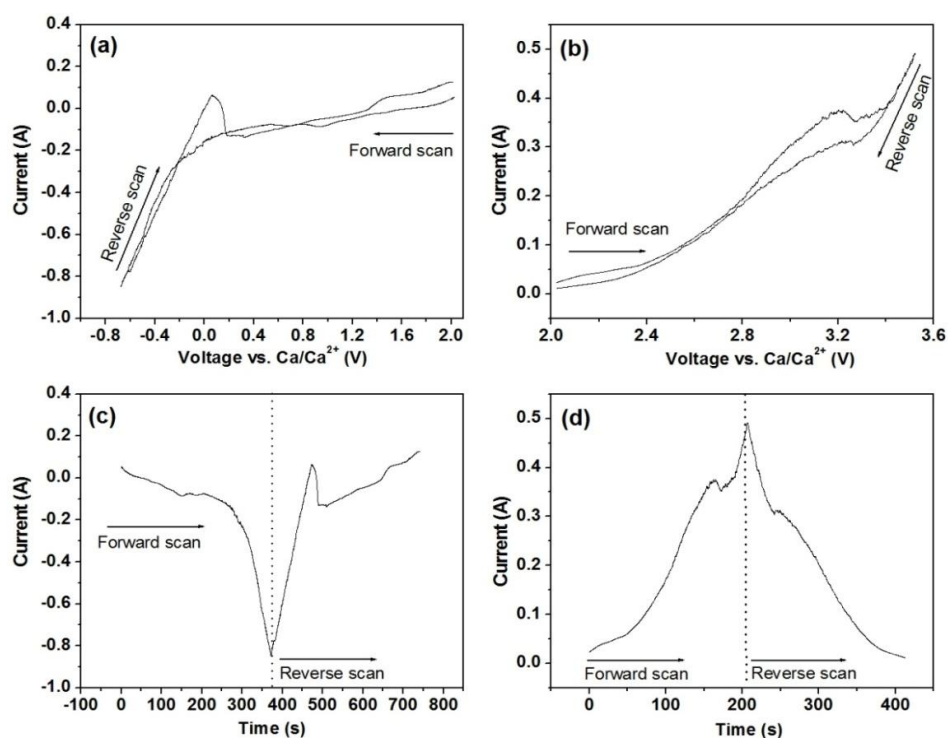


Fig. 3. Closed cyclic voltammograms (CCVs) recorded in $\text{CaCl}_2\text{-1wt.\%CaO}$ melt at 1173 K on (a) tungsten and (b) graphite working electrodes. (c) and (d) represent the corresponding open cyclic voltammograms (OCVs)

Insignificantly low current was only noticed in the OCV of tungsten working electrode for about 100 seconds and thereafter the current started to increase slowly with the applied potential. On continued polarization, the current increased linearly with applied voltage indicating the formation of calcium metal at unit activity on the electrode as per reaction (5). The graphite counter electrode potential during this period was noticed to increase rather slowly in the beginning 100 s due to adsorption of Cl^- ions on the electrode (reaction (8)) and thereafter steeply to the chlorine evolution potential of 3.2 V. The electrode behavior was similar to that observed in the CV shown in Fig. 2b. However, it can be seen from Fig. 4 that the anodic current in the beginning of calcium metal deposition on the tungsten electrode was supported by the low-energy adsorption reaction and not the chlorine evolution reaction. As the applied potential on the tungsten electrode was made more and more negative, the flux of Ca^{2+} ions discharging on the electrode was increased. This high current could not be supported by the oxidative adsorption of Cl^- ions on the graphite electrode and hence the electrode potential was automatically increased to the chlorine gas evolution potential towards

later part of the cathodic polarization. Once the scan was reversed at the switching potential of -0.3 V vs. Ca/Ca^{2+} , the cathodic current became less negative and finally became positive indicating the dissolution of the Ca metal on the tungsten electrode as



From the area (current x time) of the negative and positive charges, it is clear that the charge due to calcium dissolution by reaction (11) was significantly lower than that of calcium deposition by reaction (5). The behavior can be ascribed to the high solubility of calcium metal in the calcium chloride melt at high temperatures. The graphite electrode was polarized cathodically during this period and the electrode potential fell steeply to $\sim +0.6$ V indicating the occurrence of the reaction,



The standard formation potential of CaC_2 at 1173 K is estimated as +0.454 V [15]. The excess potential can be attributed to the IR drop of the cell ($I = \sim 0.5$ A, $R = 0.5$ Ω , $IR = 0.25$ V) at the instance of measurement.

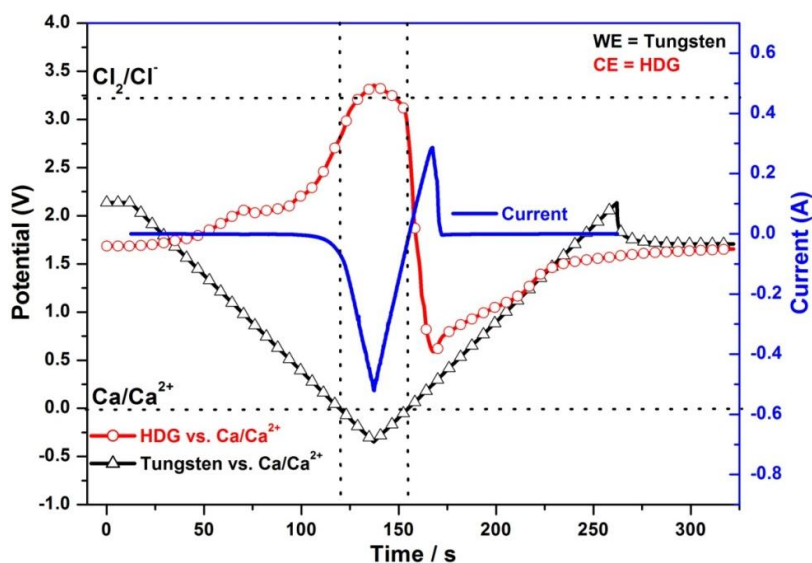


Fig. 4. The open cyclic voltammogram (OCV) of tungsten WE in CaCl_2 melt at 1173 K and the corresponding potential behavior of the high density graphite (HDG) counter electrode. The applied cyclic potential of the WE and the overall cell voltage are also shown in the figure. The horizontal dashed lines at the bottom and top of the figure represent the reversible calcium deposition and chlorine evolution potentials of CaCl_2 melt at 1173 K

3.3 CV-CEPM on $\text{CaCl}_2 - 1 \text{ wt.}\% \text{ CaO}$ Melt Using Tungsten as the WE

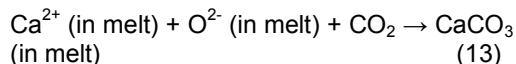
The results of the CV of tungsten electrode in CaCl_2 melt containing 1 wt.% CaO at 1173 K and the corresponding potentials of the graphite counter electrode are shown in the OCV given in Fig. 5. The OCV of the graphite counter electrode shows that the electrode potentials remained above the standard CO_2 evolution potential (1.625 V vs. Ca/Ca^{2+}) and below the chlorine evolution potential (3.231 V vs. Ca/Ca^{2+}) throughout the cathodic polarisation. The electrode potential did not increase to chlorine evolution potential even as the tungsten cathode potential was made more negative than the calcium deposition potential. The results make it amply clear that chlorine gas evolution on graphite electrode is highly unlikely during electrolysis in CaCl_2 -1 wt.% CaO melt. Evidently reaction (3) takes place on the graphite electrode. As seen before, the reaction (3) is thermodynamically a more favoured reaction than reaction (4) and hence the former reaction occurred on the electrode. As mentioned previously in section 3.1, CO_2 evolution on graphite anode is associated with high over voltage. The graphite CE potential of 2.0-2.5 V, compared to the standard potential of +1.625 V of reaction (3), in Fig. 5, is in line with this. From Fig. 5, it can be seen that the CO_2 evolution

potential is +2.5 V. A galvanostatic electro-deoxidation experiment carried out with a TiO_2 pellet cathode and graphite anode in CaCl_2 -1wt.% CaO melt showed that the anode potential was indeed >2.8 V during the entire course of the long duration electrolysis, confirming thereby that the overvoltage for reaction (3) on graphite is quite significant.

It is interesting to note a striking difference that exists between the current patterns of Fig. 4 and Fig. 5. Except during calcium deposition (forward scan) and dissolution (reverse scan), the currents on tungsten WE in pure CaCl_2 (Fig. 4) remained at insignificantly low levels suggesting thereby that the melt was devoid of any redox active impurities. But significant currents are noticed from the beginning of the cathodic polarisation of tungsten WE in CaCl_2 -1 wt.% CaO melt (Fig. 5). Similar behaviour was noticed in the CV of W working electrode in Li_2O containing LiCl melt too. Obviously the current is related to the cathodic discharge behaviour of some species like oxychlorides formed by the oxide addition to the chloride melts, but more information on this aspect is not available at in the literature.

Vishnu et al. [3,21] reported existence of high background currents in electrodeoxidation cells with graphite anode in CaCl_2 melts and attributed the currents to the redox cycling behaviour of

CO_3^{2-} ions. However, it takes time for electrolytically generated CO_2 gas to dissolve in the oxide containing melt and to form carbonate ions as per the reaction,



The species cannot be expected to form in the time scale of a typical CV experiment and hence may not be responsible to the observed current.

3.4 CV-CEPM on CaCl_2 Melt Using High Density Graphite as the WE

Fig. 6 shows the plots of CV-CEPM with a high density graphite rod (10 mm dia., area $\sim 1.10 \text{ cm}^2$) as the WE, polarized anodically, in CaCl_2 melt at 1173 K. A coil made of molybdenum wire (1 mm dia., area $\sim 9.2 \text{ cm}^2$) was used as the CE. In OCV in Fig. 6 significant current, increasing linearly with the applied potential, was observed on the graphite WE only when Cl_2 started evolving on it. It is logical to think that the calcium metal should start depositing on the CE (Mo coil) as per reaction (4) when Cl_2 gas started evolving on the graphite WE as per the reaction (5). However, it can be seen that the cell current is

supported by a cathodic reaction on the Mo CE, from $\sim +1.0 \text{ V}$ onwards and until calcium deposition at 0.00 V vs. Ca/Ca^{2+} . The underpotential currents that exist in calcium chloride melt on account of the high solubility of calcium metal as well as reaction (6) and (7) in the melt are the reasons for this behavior. This fact is very evident in the CV of tungsten electrode in CaCl_2 melt given in Fig. 2a too. As significant currents are possible at potentials much lower than that required for the calcium metal deposition, the Mo coil attained the potential close to Ca metal deposition (at unit activity) only for a very short duration towards the highest positive potential of the graphite WE electrode. This in other words means that even as chlorine evolution occurs at the graphite WE, the molybdenum CE could support the cathodic current by reactions (6) and (7). This in other words means that electrolysis of pure calcium chloride melt could generate currents at potentials lower than that required for its decomposition as calcium metal and chlorine gas. Vishnu et al. [22] reported that the underpotential calcium currents play an important role in the electrochemical reduction of oxides carried out in calcium chloride melt.

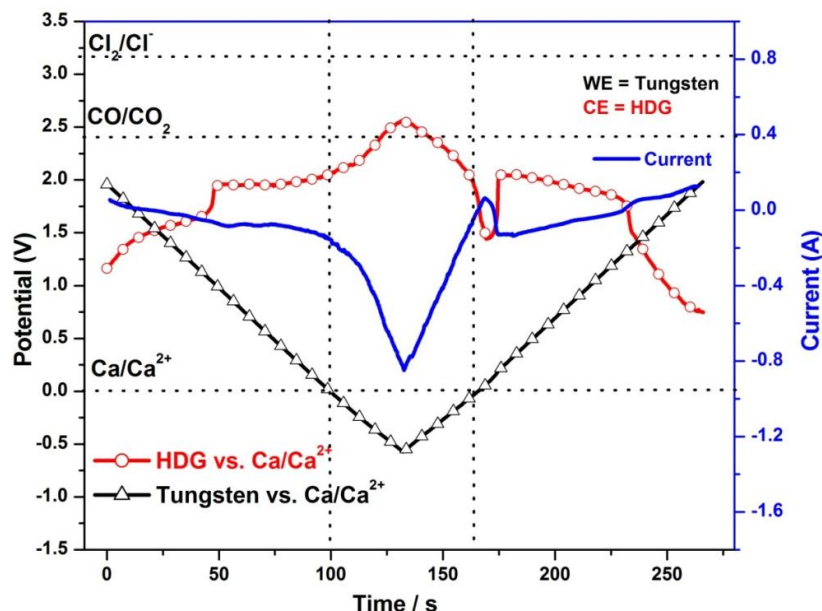


Fig. 5. The open cyclic voltammogram (OCV) of tungsten WE in CaCl_2 -1wt.%CaO melt at 1173 K and the corresponding potential behaviour of the graphite counter electrode

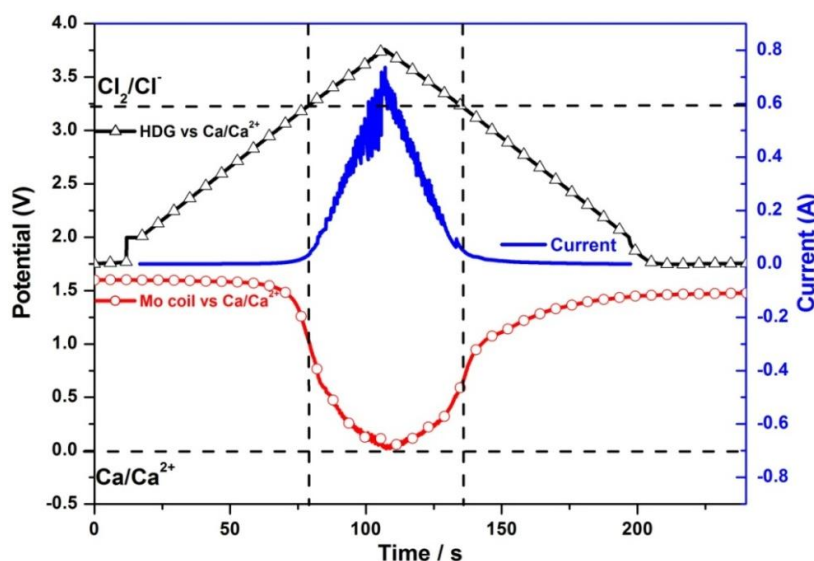


Fig. 6. The open cyclic voltammogram (OCV) of graphite WE in CaCl_2 melt at 1173 K and the corresponding potential behaviour of the molybdenum coil CE

3.5 CV-CEPM on CaCl_2 Melt Using Nb_2O_5 as the WE

Fig. 7 shows the potential behavior of graphite CE and cell current as the tip of Nb_2O_5 pellet as WE was cathodically polarized in the CaCl_2 melt. Unlike in the case of inert tungsten wire WE (Section 3.1, Fig. 2a), significant currents are generated with the Nb_2O_5 WE from the beginning of the cathodic polarization itself and the higher currents can be attributed to the high surface area of the pellet electrode. Yan and Fray [23] and Vishnu et al. [3] have studied the electro-deoxidation of Nb_2O_5 and Schwandt and Fray [24] the electro-deoxidation of TiO_2 in calcium chloride melt and proved that the cathodically polarized oxide electrode reacts with calcium ions from the electrolyte melt to form ternary calcium compounds, $\text{Ca}_x\text{M}_y\text{O}_z$ and on continued electrolysis the compounds are decomposed and deoxygenated to produce the corresponding metal (M). Formation of the calcium insertion compounds are thermodynamically more favoured than reaction (5) and hence the former reaction should occur at potentials positive to that of reaction (5). The high currents seen on the Nb_2O_5 WE at potentials positive to calcium metal deposition in Fig. 7 is related to this reaction between the electrode and the CaCl_2 melt. Vishnu et al. [3] identified different reactions occurring on cathodically polarized Nb_2O_5 electrode in CaCl_2 melt. On a typical electrolysis curve (I-t curve) the occurrence of these energetically different reactions will be shown up

as different waves. The waves seen on the cathodic current curve in Fig. 7 must, therefore, be indicating the occurrence of multiple reactions at the electrode. It is difficult to make an in depth analysis on the different reactions with the limited data available from the present electrolysis curve.

It is interesting to study the typical electrochemical behaviour of graphite CE during the cathodic polarization of the Nb_2O_5 electrode. The CE potential was seen to increase slowly from the beginning of electrolysis itself and it attained chlorine evolution potential in ~ 70 s. As discussed previously, the small anodic currents noticed before commencement of Cl_2 gas evolution on the electrode is ascribable to the oxidative adsorption of Cl^- ions on the active surface sites of the graphite electrode. As the cathodic potential was made more and more negative and higher currents are produced, the currents could not be supported by the low intensity Cl^- adsorption reaction so that the graphite CE potential was increased automatically to that of chlorine gas evolution (reaction 4) to support the current. Reversible decomposition potential of CaCl_2 is experimentally measured by using inert cathode and inert anode on which the reactions (4) and (5) take place. However, the results discussed above clearly show that when the cathode is a reactive oxide, its reaction with Ca^{2+} ions makes the potential more anodic than that required for reaction (5) so that CaCl_2 electrolyte will be

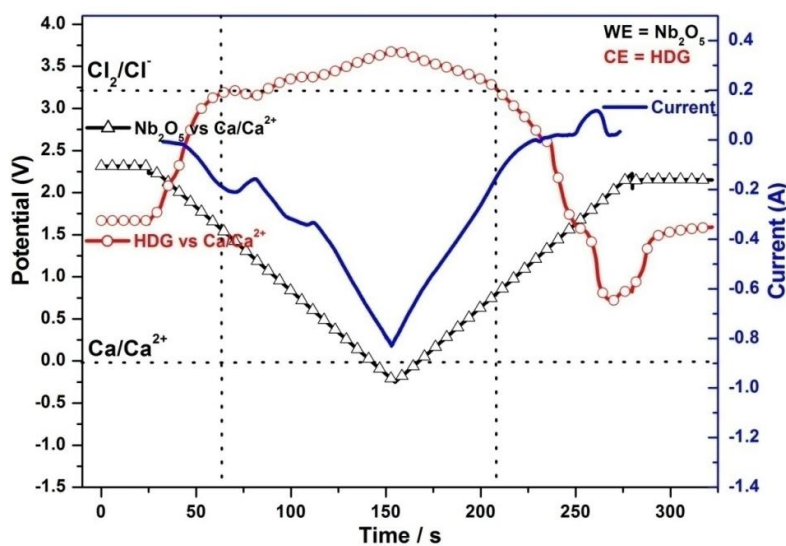


Fig. 7. The open cyclic voltammogram (OCV) of the tip of a Nb_2O_5 pellet as WE in CaCl_2 melt at 1173 K and the corresponding potential behaviour of the high density graphite (HDG) CE

electrolysed at a much lower potential than its reversible decomposition potential (3.231 V at 1173 K). In the present case, it can be seen from Fig. 7 that the chlorine gas evolution on the graphite CE commenced when the cathode potential was as low as $\sim +1.5$ V vs. Ca/Ca^{2+} as against the 0.0 V when the tungsten cathode was used (Fig. 4). This shows that chlorine gas evolution on graphite anode of a cell with oxide as the cathode (electrodeoxidation cell) can occur at $\sim +1.5$ V vs Ca/Ca^{2+} whereas the same can occur only at +3.23 V vs Ca/Ca^{2+} when the cathode of the cell is replaced with an inert metal electrode like W. The reactivity between the oxide cathode and melt thus helps to decrease the chlorine evolution voltage of the graphite anode of an electrodeoxidation cell by 1.73 V.

The electro-deoxidation of metal oxides in molten salts via the FFC Cambridge process was reported to occur via the oxygen ionization mechanism at the melt - oxide - electronic conductor three phase interlines [6,25]. Generally a cell voltage of 3.0 V or 3.1 V is applied to the electrodeoxidation cells in the FFC Cambridge process assuming that the voltage will be insufficient to decompose the CaCl_2 melt (decomposition potential 3.231 V at 1173 K) [26]. But the present finding shows that the applied potential of 3.0 or 3.1 V will be good enough to decompose the melt and to produce chlorine gas on the graphite counter electrode. Mohandas et al. [10] investigated the electrochemical reduction of TiO_2 in CaCl_2 melt at 1173 K at 3.1 V

and the results showed that the graphite anode potential remained at or above chlorine evolution potential throughout the course of the electrodeoxidation experiment. Schwandt and Fray [24] also reported presence of chlorine gas at graphite anode during electro-deoxidation of TiO_2 pellet electrodes in CaCl_2 melt.

4. CONCLUSION

The counter electrode (CE) potentials of a typical cyclic voltammetry measurement are not used in any analysis of the system and hence not measured. However, the counter electrode potential measurements carried out on CV cells with CaCl_2 and CaCl_2 -1wt.% CaO as electrolyte melts do show that the data can in fact be used to gain information on the counter electrode reactions and hence in the comprehensive assessment of the cell reactions. The measurements carried out on a typical FFC cell configuration with a Nb_2O_5 pellet working electrode placed against graphite counter electrode in CaCl_2 melt showed that chlorine gas evolution on the graphite electrode can take place at a very low cell voltage (1.5 V) compared to the decomposition potential of the melt at 3.23 V. Electrodeoxidation in the FFC process is generally carried out at ~ 3.0 V and the present finding makes it very clear that the CaCl_2 melt will be decomposed and chlorine gas liberated on the graphite anode at this cell voltage. The results further show that it is required to add CaO to the melt to suppress the anodic chlorine gas

evolution and to favour the CO/CO₂ evolution on the graphite anode. The advantage of the novel measurements presented in this study is that significant information on multiple electrode processes occurring in an electrochemical cell like an electro-deoxidation cell, which could otherwise be obtained only from different experiments, could be obtained in a single experiment so that a quick assessment of the process can be made.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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