Cyclic Voltammetry for Monitoring Corrosive Impurities in Molten Chlorides for Thermal Energy Storage

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Abstract

Molten chlorides are promising alternative thermal energy storage (TES) materials to be applied in concentrating solar power (CSP) plants. Their high thermal stability makes them appropriate candidates to replace the commercial TES materials in CSP, nitrate salts (stable up to 550 °C), when higher operating temperatures (e.g., 700 °C) are required for higher efficiency of energy conversion. However, the application of molten chlorides at higher temperatures causes increased corrosiveness of containers and structural materials. In this work, cyclic voltammetry (CV) is applied to measure the concentration of corrosive oxide/hydroxide impurities in the molten chlorides *in-situ*, in order to assist the corrosion control. Before the electrochemical experiments, pre-electrolysis (PE) was performed on molten $MgCl_2/KCl/NaCl$ (60/20/20 mole%) salts to remove most of the impurities including oxide/hydroxide. By fitting the CV data from PE with those from the acid consumption (AC) measurements on the simultaneously collected salt samples, the parameter for the calculation of the concentration of $MgOH^+$ from the peak current density was determined under the conditions 500 °C and sweep rate of 200 mV/s. By adding NaOH pellets into the molten salts, a significant change of a peak was observed in the cyclic voltammograms due to the concentration change of the most stable hydroxide species $MgOH^+$. Moreover, when the determined parameter was used in the calculation of the concentrations of $MgOH^+$ from the peak current densities, the calculated concentrations of $MgOH^+$ compare well with those from AC.
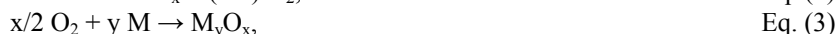
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1. Introduction

Molten chloride salt mixtures such as $MgCl_2/KCl/NaCl$ are promising thermal energy storage (TES) and heat transport fluid (HTF) materials to be applied in concentrating solar power (CSP) plants. Their high thermal stability makes them appropriate candidates to replace the commercial TES materials in CSP - nitrate salt mixtures (stable up to 550 °C), when higher operating temperatures are required (up to 700 °C) for higher efficiency of thermal to electrical energy conversion [1].

However, the application of molten chloride salts at higher temperatures causes additional challenges such as increased corrosiveness of containers and structural materials [1-3]. It is well accepted that the corrosion rates significantly depend on the concentration of oxide/hydroxide impurities in the molten chloride salts [1-3]. The corrosive impurities are mainly produced from water and oxygen existing in the chloride salts, as well as moisture and oxygen in the atmosphere above the chloride salts [1-5]. The presence of water in the chloride salts from hydrated phases, e.g., strong hydrophilic chloride salt - $MgCl_2$, induces its hydrolysis during heating following the simplified equation Eq. (1), and the corrosion of the metal alloys of containers and structural materials according to Eq. (2), while oxygen containing species existing in the chloride salts (e.g. O_2) corrodes the containers and structural materials by oxidizing the alloying components as shown in the simplified equation Eq. (3) [4-6].

$$MgCl_2 + H_2O \rightarrow MgO + 2\ HCl, \qquad \text{Eq. (1)}$$
$$x\ HCl + M \rightarrow MCl_x + (x/2)\ H_2, \qquad \text{Eq. (2)}$$
$$x/2\ O_2 + y\ M \rightarrow M_yO_x, \qquad \text{Eq. (3)}$$

where M represents the alloying components in the metal alloys.

Considerable effort has been made to control the concentrations of corrosive oxide/hydroxide impurities to reduce the corrosion effect of the molten chloride salts [4-12]. For instance, it is reported in [4-5] that when the heating of the salts with strong hydrophilic $MgCl_2$ in the dehydration process is carefully performed, the irreversible decomposition side reactions to the corrosive components HCl and MgOHCl (Eq. (4)) or MgO (Eq. (5)) can be controlled at a low level. Thus, only a small amount of oxide/hydroxide impurities remains in the salts.

$$MgCl_2·2H_2O \rightarrow MgOHCl + HCl, \qquad \text{Eq. (4)}$$
$$MgCl_2·2H_2O \rightarrow MgO + 2\ HCl. \qquad \text{Eq. (5)}$$

Furthermore, in order to reduce the corrosive impurities remaining in the molten salts after the dehydration process further regarding to the corrosion rate, some techniques [6-12] to purify the salts have been developed. In literature, purification was accomplished by a chlorinating process (CCl_4, HCl, or some other chlorinating compound [7-9]), or by reduction of the salt by using active metals such as Mg [10], or saturation of a salt with a liquid metal (i.e., LiCl with Li metal [6, 11, 12]), to reduce redox potential of the melt.

For an efficient control of oxide/hydroxide impurity concentrations in molten salts in industry, reliable, fast but affordable concentration measurements of these impurities are required and essential. At the start of this work, measurements of oxide/hydroxide in industrial systems with *ex-situ* analytical methods were well advanced [13]. Compared to these *ex-situ* methods generally *via* collecting and analyzing a salt sample out of the melt, *in-situ* measurements of oxide/hydroxide with an electrochemical analysis system based on cyclic voltammetry provide unique possibility to monitor the concentration and control the technological processes [14]. Some electrochemical investigations to examine oxide/hydroxide species in chloride melts such as $MgCl_2/NaCl$ (730-850°C) [13], LiCl/KCl (350-500°C) [15] and (430-500°C) [16] had been performed. In many papers [14-18], it was found that in melts such as $MgCl_2/NaCl$, LiCl/KCl, $CaCl_2/KCl$ the height of the oxide-ion's oxidation peak, as well as the hydroxide species' reduction peak, was directly proportional to the concentration of oxide/hydroxide species, respectively.

To our knowledge, no published papers are available which investigate the correlation between the oxide-ions oxidation peak and the hydroxide species reduction peak with the concentrations of corrosive oxide/hydroxide species in $MgCl_2/KCl/NaCl$ in the temperature range of 500-700 °C, which is a promising TES and HTF material in CSP and other power plants. In this work, we focus on understanding the electrochemical behavior of $MgCl_2/KCl/NaCl$ with the oxide/hydroxide impurities *via* the CV experiments, which is essential for the *in-situ*

measurements of the concentrations of oxide/hydroxide by analyzing the cyclic voltammograms.

2. Experimental

2.1. Chemicals

KCl(99%) and NaCl(99%) were purchased from Alfa Aesar, while anhydrous $MgCl_2$(99%) came from Magnesia, a global distribution company of Magnesium based compounds in Germany. They were used to make the eutectic salt mixture of $MgCl_2$/KCl/NaCl (in this work with the molar composition of 60/20/20). According to our previous work [5], the heating process of the salts is performed as follow: after vacuuming for 30 minutes ($\leq$ 30 mbar), the salt mixture was heated under an argon atmosphere (purity $\geq$ 99.9999%, $H_2O \leq$ 0.5 ppm, 20 qnl/h, pressure above atmospheric pressure is about 0.1 bar) to 200 °C with the heating rate of 5°C/min, then kept at 200 °C for 1 hour, and after that was heated to the studied temperature of the electrochemical experiments, i.e., 500 °C. The titration measurements, which are described in section 2.4., show that the concentration of oxygen species in the salts after the heating process was less than 0.6 mol/kg(salt). Since literature [13] and [18] shows that the solubility of MgO in $MgCl_2$/NaCl was only 72-75 ppm O (4.6×10^{-3} mol/kg(salt)) at 730 °C, the concentration of oxide ions was neglected in the titration measurements. NaOH (pellet, 99%) purchased from Alfa Aesar was added in the molten salts to change the concentration of hydroxide species in the salts, in order to study the correlation between the peak current densities and concentrations of hydroxide species.

2.2. Experimental set-up

Figure 1 shows a schematic of the experimental set-up used for CV experiments. A high temperature resistance glassy carbon crucible purchased from HTW Germany (Sigradur® G) was used to avoid the reaction of the molten salts with the materials of the crucible. During the experiments, the temperature of the molten salts under an argon atmosphere (same parameters as mentioned in section 2.1.) was controlled by the programmable furnace and the thermocouple close to the surface of the molten salt. As shown in Figure 1, an Al_2O_3 plate was used below the crucible to insulate the electrical contact between the crucible and the steel tubing during the CV experiments. The pure tungsten wires purchased from Alfa Aesar (99.95 %, diameter: 1 mm) were applied in this work as the working, counter and reference electrodes for the concentration measurements on hydroxide species, while glassy carbon electrodes from HTW Germany (diameter of 4 mm) were used as the working electrodes for oxide species.

Using the sample collector (Figure 1), salt samples were collected directly before the CV measurements for analysis. The oxide/hydroxide concentrations in the salt samples were determined by the acid consumption method based on titration [5]. The sample collector consists of a quartz tube with an inner diameter of 4 mm and a plastic header. Before immersion of the quartz tube into the melt, the plastic header was removed. So the quartz tube would be swept by the argon gas due to the over pressure in the metal tubing. After that, there was no air with moisture in the quartz tube. Then the plastic header was put on the quartz tube again. After immersion of the quartz tube into the melt, the molten salts were sucked into the quartz tube by pressing and releasing the plastic header. During taking the sample collector out of the metal tubing, the molten salts were cooled down to be solid. Depending on the size of the plastic header, various amounts of the salts can be collected. In our experiments, about 2 g salt was collected every time for the acid consumption experiments.

2.3. CV experiments for oxide/hydroxide concentration measurements

During the CV experiments, the working, counter and reference electrodes were immersed into the molten salts. The immersion depth of the working electrode was fixed to 5 mm (i.e., the contact area of the tungsten and glassy carbon working electrode with the melt is 16.5 and 75.4 mm^2, respectively), while the counter and reference electrodes had a contact area of about 30 mm^2, as shown in Figure 1. The CV experiments were conducted using a ZENNIUM electrochemical workstation from Zahner GmbH (Germany).

Using the tungsten working electrode, a typical obtained cyclic voltammogram in our work is given in Figure 2 to show a current response of the electrochemical reactions in molten salts. As literature [13], [19] concludes that the

most stable H-containing positive ion is Magnesium hydroxyl ($MgOH^+$), the peaks A, A', B and C in the cyclic voltammogram are considered to represent the following electrochemical reactions, respectively:

$$\text{Reaction A: } Mg^{2+} + 2e^- = Mg \qquad\qquad \text{Eq. (6)}$$
$$\text{Reaction A': } Mg = Mg^{2+} + 2e^- \qquad\qquad \text{Eq. (7)}$$
$$\text{Reaction B: } MgOH^+ + e^- = MgO + \tfrac{1}{2} H_2 \qquad\qquad \text{Eq. (8)}$$
$$\text{Reaction C: } Cl^- = \tfrac{1}{2} Cl_2 + e^- \qquad\qquad \text{Eq. (9)}$$

According to literature [13], the bulk concentration of the reacting species in salts, $c^\infty(MgOH^+)$ in mol/kg(salt), is proportional to the peak current density of the peak B, $i_p(B)$ in mA/cm²:

$$c^\infty(MgOH^+) = k(T, v) \cdot i_p(B), \qquad\qquad \text{Eq. (10)}$$

$k(T, v)$: the factor in mol cm²/mA/kg(salt), which depends on the temperature T in K and potential sweep rate v in V/s. Thus, in this case, the peak current density of the peak B can simply be used to *in-situ* detect the concentration of the impurity hydroxide in the molten salts.

As shown in Figure 3, the CV measurements in this work show that the plot of $i_p(B)$ vs. $v^{1/2}$ is linear and passes through the origin when the sweep rate v is below 500 mV/s. Thus, a sweep rate of 200 mV/s was used in all other CV experiments in this work.
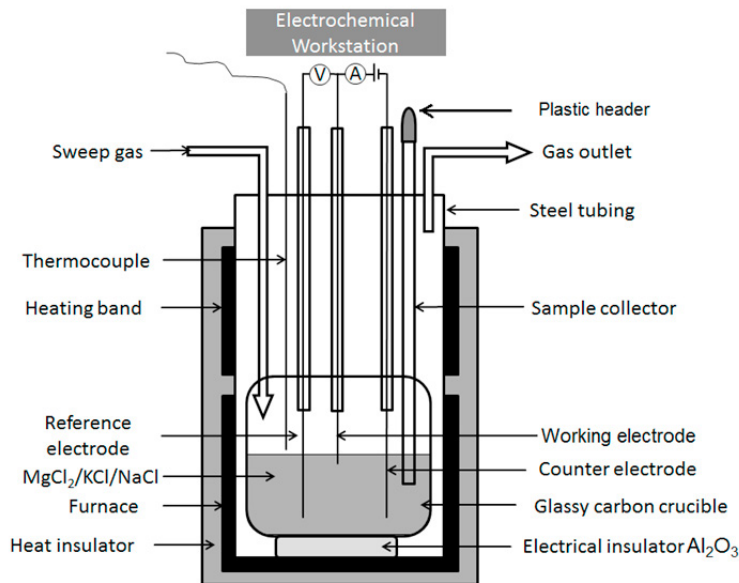

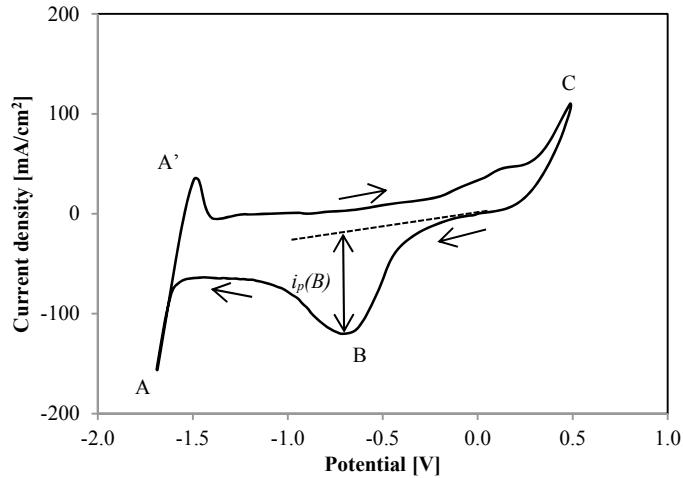Figure 1: Schematic of experimental set-up for cyclic voltammetry experiments on molten salts MgCl₂/KCl/NaCl.

Figure 2: Cyclic voltammogram obtained on a tungsten electrode in $MgCl_2/KCl/NaCl$ (60/20/20 mole%) at 500 °C. Sweep rate: 200 mV/s. Tungsten reference. $i_p(B)$: peak current density for reaction B.
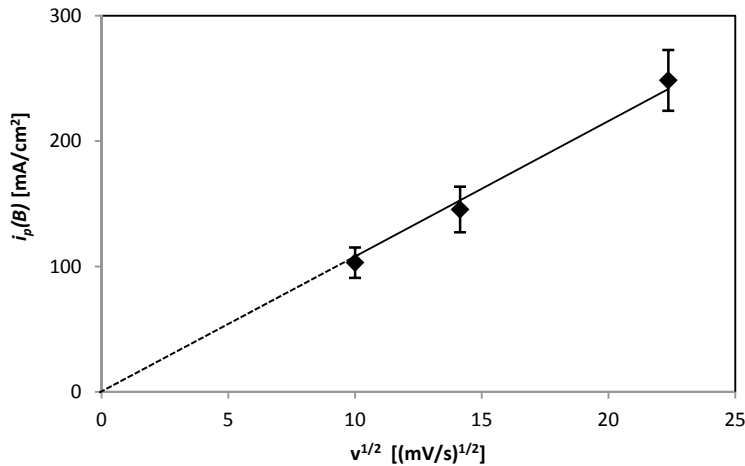

Figure 3: Peak current density of hydroxide reduction reaction versus the sweep rate of CV diagrams. Working electrode is tungsten. T = 500 °C.

2.4. Acid consumption for oxide/hydroxide concentration measurements

In order to evaluate the CV data, an acid consumption based titration was used to determine the total amount of oxide/hydroxide in a salt sample. The sample (m_{sample} = 0.5-1 g) was dissolved in a known amount of HCl (10 ml 0.1 M HCl solution). The dissolution reactions are:

$$O^{2-} + 2HCl = 2Cl^- + H_2O, \qquad\qquad\qquad \text{Eq. (11)}$$
$$MgOH^+ + HCl = Mg^{2+} + Cl^- + H_2O. \qquad\qquad\qquad \text{Eq. (12)}$$

The excess HCl is titrated with NaOH solution (0.1 mol/L, V_{NaOH}). The titration indicator is 1% phenolphthalein solution. As mentioned in section 2.1., it was considered that all the amount of the reacted HCl was due to the dissolution reaction with $MgOH^+$. Thus, the concentration of $MgOH^+$ in the salt sample can be calculated as follow:

$$C(MgOH^+) \text{ [mol/kg(salt)]} = (C_{HCl}*V_{HCl} - C_{NaOH}*V_{NaOH}) /m_{sample}, \qquad\qquad \text{Eq. (13)}$$

where C_{HCl} and C_{NaOH} are 0.1 mol/L (1×10^{-4} mol/ml), V_{HCl} is the volume of HCl, 10 ml, V_{NaOH} is the titration volume of NaOH in ml; m_{sample} is the mass of the salt sample in kg.

3. Results and discussion

3.1. Pre-electrolysis and determination of constant $k(T,v)$

As introduced in section 2.1, 140 g salt mixtures $MgCl_2$/KCl/NaCl were heated to the temperatures for CV experiments. The acid consumption experiments and CV experiments on the molten salts show that there was still a small amount of impurities in the melts, although pure (purity > 99%) anhydrous $MgCl_2$, KCl and NaCl were used. The acid consumption experiments show that the amount of oxygen based impurities is about 0.6 mol/kg(salt) at 500 °C. The cyclic voltammogram in Figure 4 shows obvious noise probably due to the impurities besides oxide/hydroxide in the molten salts, as well as an obvious peak at approx. +1.0 V *vs*. Mg/Mg^{2+}(i.e., 1.0 V more positive than the peak of $MgCl_2$ decomposition (Mg/Mg^{2+}) as shown in Figure 4), which represents hydroxide reduction reaction (Eq. (8)).
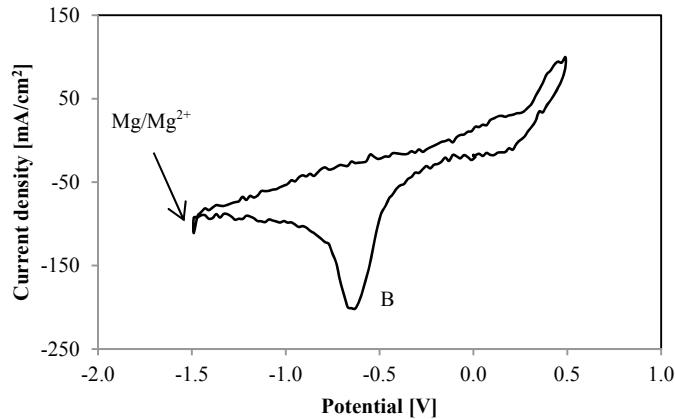

Figure 4: Cyclic voltammogram of molten salt $MgCl_2$/KCl/NaCl (60/20/20 mole%) recorded directly after heating to 500 °C. Working, counter and reference electrodes are tungsten. Sweep rate: 200 mV/s.

In order to remove the noise in the cyclic voltammograms, literature [13], [16] suggests the pre-electrolysis (PE) to reduce the impurities. In this work, PE of 5 and 20 min was performed successively. The tungsten electrodes were used as the working, counter and reference electrodes, while the voltage between the working and counter electrode was –2V (counter electrode = reference electrode). The cyclic voltammograms after PE are shown in Figure 5. After 5 min PE, the noises in CV disappeared, while the peak for hydroxide (Peak B) was still obvious. Further PE could reduce the concentration of hydroxide significantly, but not remove it completely. Thus, in other experiments in this work, 25 min PE was performed to pre-treat the melts.

As shown in Eq. (10), the concentration of $MgOH^+$ can be calculated from the current density of the peak for $MgOH^+$ by multiplying the factor $k(T,v)$. Thus, in order to determine the factor k, the concentrations of $MgOH^+$ determined from CV measurements ($c_i^{CV} = k(T,v) \cdot i_p^i(B)$) were fitted with those from the acid consumption method c_i^{AC} *via* the least square method, i.e., solving the following equation:

$$\sum_{i=1}^{n} \left(c_i^{CV}(k) - c_i^{AC} \right)^2 = \sum_{i=1}^{n} \left(k(T,v) \cdot i_p^i(B) - c_i^{AC} \right)^2 = \text{minimal,} \qquad \text{Eq. (14)}$$

where n is the total number of the data considered here. The factor k for $MgOH^+$ in $MgCl_2$/KCl/NaCl (60/20/20 mole%) under the conditions 500 °C and sweep rate of 200 mV/s was determined to be $3\pm1\times10^{-3}$ mol cm^2/mA/kg(salt). The best fit of the concentrations of $MgOH^+$ from the CV and AC method is shown in Figure 6.
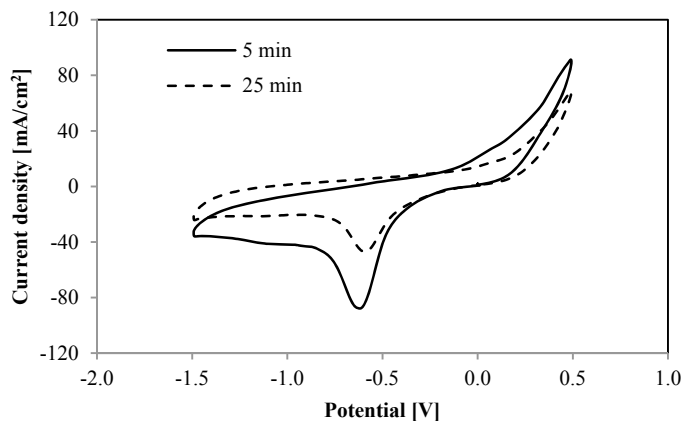
Figure 5: Cyclic voltammograms of molten salts after 5 (solid line) and 25 (dotted line) minutes direct current pre-electrolysis at 500 °C. The voltage on the working and counter electrodes are kept at -2 V. Sweep rate: 200 mV/s.
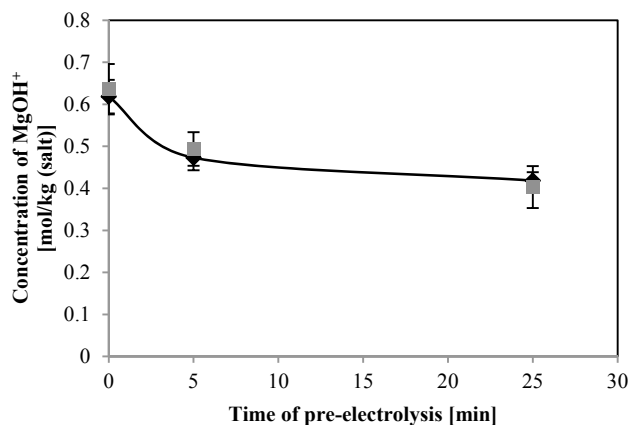

Figure 6: Concentrations of corrosive impurity MgOH$^+$ in molten salt over the time of pre-electrolysis under –2 V, which were determined with the CV (black curve) and acid consumption (grey points) method, respectively. Error bars represent the standard deviations in the CV and acid consumption measurements (three measurements). Working electrode is tungsten. T = 500 °C.

3.2. CV experiments after adding NaOH

1.5 g NaOH (0.0375 mol) was added into 140 g molten salt direct after the pre-electrolysis. Figure 7 shows selected cyclic voltammograms at different time after adding NaOH. The current densities of the peak relating the concentration of MgOH$^+$ at different time were obtained directly from the cyclic voltammograms and are summarized in Table 1, together with the corresponding concentration of MgOH$^+$, which are calculated from the peak current densities by multiplying the determined factor $k(T, \nu)$. It was observed that the current density (i.e. the concentration of MgOH$^+$) increases initially. After fifteen minutes, it starts to decrease. This implies that the dissolution of the added NaOH and the decomposition of MgOH$^+$ (derived from NaOH) to MgO occur simultaneously. In literature [13], MgOHCl pellets were added to the MgCl$_2$/NaCl melt at 730-850 °C for changing the concentration of MgOH$^+$ in the melt. The concentration of MgOH$^+$ started to decrease after an hour. It may be explained that MgOHCl dissolves more slowly than NaOH.
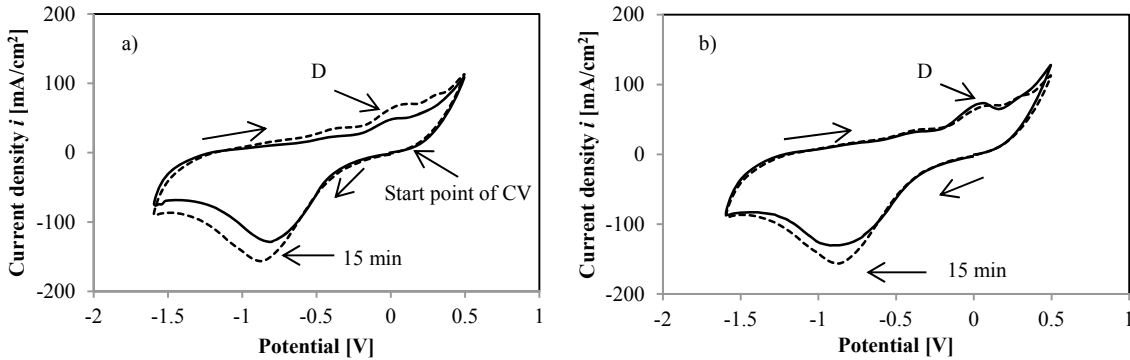
Figure 7: Cyclic voltammograms after adding NaOH in the molten salts: a) 0 min (solid) and 15 min (dotted); b) 15 min (dotted) and 60 min (solid). T = 500 °C. Working electrode: tungsten. Sweep rate: 200 mV/s. 0 min means the measurement directly after adding NaOH.

Figure 8 shows the concentration of $MgOH^+$ as a function of time after adding NaOH. The concentration of $MgOH^+$ (black curve) were calculated from the CV data by multiplying the determined factor $k(T, v)$ for $MgOH^+$, while the grey points represent the concentrations of $MgOH^+$ obtained with the AC method. A good correlation of the concentrations of $MgOH^+$ from these two methods can be found. Moreover, the increased concentration of $MgOH^+$ within 15 min after adding NaOH is about 0.2 mol/kg(salt), which is slightly less than the added amount of NaOH (0.27 mol/kg(salt)). This also indicates that the dissolution of the added NaOH and the decomposition of $MgOH^+$ derived from NaOH may occur simultaneously.

Interestingly, an obvious peak D was observed in the anodic range of the cyclic voltammograms (see Figure 7), which has not been reported in literature. Further analysis is required to study the electrochemical nature of this peak.

Table 1: Change of peak current densities of $MgOH^+$ reduction reaction and the corresponding concentration of $MgOH^+$ after adding NaOH. t = 0 represents the measurement directly after adding NaOH.

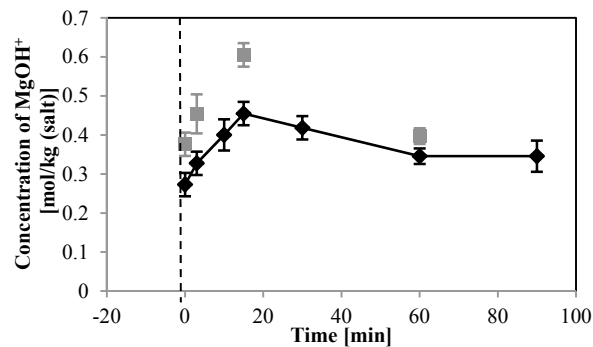| Time t (min)	Current densities [mA/cm^2]	C($MgOH^+$) calculated [mol/kg(salt)]
0	91±10	0.27±0.03
3	109±10	0.33±0.03
10	133±13	0.40±0.04
15	**152±10**	**0.46±0.03**
30	139±10	0.42±0.03
60	115±7	0.35±0.02
90	115±13	0.35±0.04

Figure 8: Concentration of $MgOH^+$ (black points and curve: CV data; Grey points: titration data) as a function of time after adding 1.5 g NaOH (0.27 mol/kg(salt)). Error bars represent the standard deviations in the CV and acid consumption measurements (three measurements).

4. Conclusions

In order to monitor the concentration of corrosive oxide/hydroxide impurities in the chloride molten salts with an electrochemical method based on cyclic voltammetry, the correlation between the peak current densities and concentrations of oxide/hydroxide species was investigated. To evaluate the concentrations of oxide/hydroxide species obtained from the electrochemical method, a sample collection system was built for the determination of the concentration of impurities with the acid consumption titration method.

As an anhydrous $MgCl_2$ purchased from a global distribution company was used, the chloride salt mixtures were purified with pre-electrolysis for cyclic voltammograms without noises prior to the CV experiments. Based on the CV data from pre-electrolysis experiments, the parameter for the calculation of the concentration of $MgOH^+$ ion from the peak current density under the conditions 500 °C and sweep rate of 200 mV/s was determined.

After pre-electrolysis, NaOH was added in the molten salt to change the concentration of $MgOH^+$. A significant change of the peak for the reduction reaction of $MgOH^+$ was observed in the cyclic voltammograms. When the determined parameter based on the CV data from pre-electrolysis experiments was used in the calculation of the concentrations of $MgOH^+$ from the current density of the peak for the reduction reaction of $MgOH^+$, the calculated concentrations of $MgOH^+$ from the CV data compare well with those from the acid consumption titration method.

Overall, this work presented the successful commissioning of an experimental setup to study molten chlorides *in-situ* (by cyclic voltammetry) and *ex-situ* (post-analysis of salt samples by titration). Correlation between both methods could be established. This will allow for further studies of the molten salt chloride chemistry and development of the process technology for thermal energy storage systems up to 700 °C in future.

Acknowledgements

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