Electrochemical measurement of 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 concentrated solar power (CSP) plants owing to their higher thermal stability (stable at $>800\,°C$) than the commercial TES materials – nitrate salt mixtures (decomposed at $\sim550\,°C$). Higher operating temperatures of TES can increase efficiencies of thermal into electrical energy conversion for CSP power plants, but cause additional challenges, particularly increase corrosiveness of metal containers and structural materials. Corrosion rates significantly depend on concentration of corrosive hydroxide impurity in the molten chlorides. This paper presents an electrochemical method based on cyclic voltammetry (CV) to *in-situ* measure the concentration of the hydroxide impurity in molten $MgCl_2$/KCl/NaCl (60/20/20 mol%) salts at 500–700 °C. Before each CV experiment, the concentration of the hydroxide impurity in the molten salts was measured *via* acid consumption (AC) measurements on the simultaneously collected salt sample. The results of CV and AC experiments show that the peak current densities obtained from CV are proportional to the concentrations of the hydroxide impurity obtained from AC in the studied system. The slopes of peak current densities *vs.* concentrations of the hydroxide impurity are determined, which compare well with literature data. This electrochemical method for monitoring the corrosive hydroxide impurity is expected to assist the corrosion control on containers and structural materials in the molten chlorides.

1. Introduction

Concentrated solar power (CSP) technology is emerging as one of the important technologies in the future renewable energy system. CSP plants concentrate a large area of sunlight onto a small area by using mirrors or lenses to generate solar power. Electricity is generated when the concentrated light is converted to heat, which drives a heat engine connected to an electrical power generator. Heat storage in molten salts, *e.g.*, commercial nitrate salt mixtures, allows CSP plants to generate dispatchable power during the absence of sunlight and adds value to such power plants when compared to photovoltaic panels. It is reported that global installed CSP-capacity has increased nearly fifteen-fold from 2005 to 2015 (up to 4.8 Gigawatts) and grew at an average rate of 50 percent per year from 2010 to 2015 [1].

Molten chloride salt mixtures such as $MgCl_2$/KCl/NaCl (melting temperature: $\sim380\,°C$) are promising thermal energy storage (TES) materials to store the heat from sunlight in CSP plants, due to their high thermal stability, good thermal conductivity, high heat capacity but low price, as summarized in Table 1 together with the properties of other common TES materials. In particular, 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 (*e.g.*, 700 °C) for higher efficiency of thermal to electrical energy conversion [2].

However, the application of molten chloride salts at higher temperatures causes additional challenges, particularly increased corrosiveness of containers and structural materials [2,3,7–10]. Table 2 summarizes the corrosion rates of commercial steels and Ni-based alloys in various molten salts at different temperatures [3,7]. When using the molten chloride salts (*e.g.*, $ZnCl_2$/KCl/NaCl) at high temperatures, *e.g.*, 800 °C, even using expensive Ni-based alloys with high corrosion resistance (*e.g.*, Hastelloys C-22 and C-276) cannot meet the requirements of corrosion resistance in

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Table 1
Properties of commonly used molten salts as TES in CSP [3–3–6].

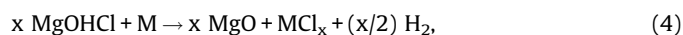| Molten salts composition (wt.%)	Melting point (°C)	Stability limit (°C)	Viscosity (mPa s)	Density (g cm^{-3})	Heat capacity (kJ kg^{-1} K^{-1})	Cost ($/kg)
Solar Salt NaNO$_3$/KNO$_3$ (60/40)	220 [3]	600 [3]	3.26 [3] (300 °C)	~1.84 [4]	~1.5 [4] (560 °C)	0.5 [3]
Hitec NaNO$_3$/KNO$_3$/NaNO$_2$ (7/53/40)	142 [3]	535 [3]	3.16 [3] (300 °C)	~1.9 [4]	1.56 [3] (300 °C)	0.93 [3]
LiNaK carbonates Li$_2$CO$_3$/Na$_2$CO$_3$/K$_2$CO$_3$ (32.1/33.4/34.5)	~400 [3]	800–850 [3]	4.3 [3] (800 °C)	1.85 [4]	~1.4–1.5 [3]	~1.2–1.3 [3]
LiNaK fluorides KF/LiF/NaF (59/29/12)	454 [4]	>700 [4]	N/A	1.89 [4]	1.89 [4] (700 °C)	>2[a]
ZnNaK chlorides ZnCl$_2$/NaCl/KCl (68.6/7.5/23.9)	204 [3]	850 [3]	4 [3] (600–800 °C)	~2 [5]	0.81 [3] (300–600 °C)	<1 [3]
MgNaK chlorides MgCl$_2$/NaCl/KCl (68.2/14.0/17.8)	380 [6]	>800	4 [5] (500–800 °C)	~1.65 [5]	~1.0 [5] (500–800 °C)	<0.5[a]

[a] The prices of LiNaK fluorides and MgNaK chlorides are estimated from the data on www.alibaba.com.

Table 2
Corrosion in commonly used molten salts as TES [3,7].

Molten Salts	Alloy	Temperature (°C)	Corrosion rate in inert gas (μm/year)	Refs.
Solar Salt	SS 316	600	15.9	[3]
	Ha230	600	47	[3]
Hitec	SS 321	570	2	[3]
LiNaK carbonates (32.1/33.4/34.5)	In600	900	<1000	[3]
ZnNaK chlorides (68.6/7.5/23.9)	SS 304	800	110–200	[7]
	SS 304	500	>300 (in air)	[7]
	Ha C-22	800	<50	[7]
	Ha C-276	800	<50	[7]

industrial applications (corrosion rate <10 μm/year). In addition, the concentration of corrosive impurities in the molten chloride salts should be controlled.

It is well known that corrosion rates significantly depend on the concentration of hydroxide/O$_2$ impurities in the molten chloride salts [2,8,9]. The corrosive impurities are mainly produced from water and O$_2$ existing in the chloride salts, as well as moisture and O$_2$ in the atmosphere dissolving in the chloride salts [2,8–11]. 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 equations Eqs. (1) and (2) to produce the corrosive HCl and MgOHCl (more details shown in Eqs. (6) and (7)). HCl and MgOHCl have corrosion reactions with the metal alloys of containers and structural materials according to the simplified equations Eqs. (3) and (4), while oxygen containing species existing in the chloride salts (*e.g.* dissolved O$_2$) corrode the containers and structural materials by oxidizing the alloying components as shown in the simplified Eq. (5) [11,12]. Table 2 shows that when the molten ZnCl$_2$/NaCl/KCl salt is exposed in air, which leads to a high concentration of dissolved O$_2$ and hydroxide species in melt, the corrosion rate of steel 304 at 500 °C is much higher than that at 800 °C when sweeping the molten salt with an inert gas.

$$MgCl_2 + H_2O \rightarrow MgO + 2\,HCl, \tag{1}$$

$$MgCl_2 + H_2O \rightarrow MgOHCl + HCl, \tag{2}$$

$$x\,HCl + M \rightarrow MCl_x + (x/2)\,H_2, \tag{3}$$

$$x\,MgOHCl + M \rightarrow x\,MgO + MCl_x + (x/2)\,H_2, \tag{4}$$

$$x/2 O_2 + y\,M \rightarrow M_yO_x, \tag{5}$$

M = the alloying components in the metal alloys.

Considerable effort has been made to control the hydrolysis during heating to reduce the corrosion effect of the molten chloride salts [10–18]. For instance, it is reported in [10,11] that when the heating of the salts with strong hydrophilic MgCl$_2$ in the dehydration process is carefully performed, the irreversible decomposition side reactions producing MgOHCl and MgO (see Eqs. (6) and (7)) can be suppressed substantially. Only a small amount of oxide/hydroxide impurities remains in the salts, *i.e.*, a small amount of corrosive HCl and MgOHCl is produced.

$$MgCl_2 \cdot H_2O \rightarrow MgOHCl + HCl, \tag{6}$$

$$MgCl_2 \cdot H_2O \rightarrow MgO + 2\,HCl. \tag{7}$$

MgOHCl dissolved in molten salts can be decomposed further to MgO and corrosive HCl at high temperatures. Therefore, to reduce the corrosive impurity ion MgOH$^+$ in molten salts further to an acceptable concentration level regarding to the corrosion rate (the experimental study on the acceptable concentration level in MgCl$_2$/KCl/NaCl is in progress in our work), some techniques [12–18] to purify the salts have been developed. In literature, purification was accomplished by a chlorinating process (CCl$_4$, HCl, other chlorinating compounds [12–14]), by reduction of the salt by using active metals such as Mg [15], or saturation of a salt with a liquid metal (*i.e.*, LiCl with Li metal [16–18]), to reduce the redox potential of the melt.

For an efficient control of corrosive impurity concentrations in molten salts in industrial applications, reliable, fast but affordable concentration measurements of the corrosive impurities are required. At the start of this work, hydroxide containing ions in molten chlorides were examined with *ex-situ* analytical methods [19]. However, compared to these *ex-situ* methods, generally *via* collecting and analyzing a salt sample out of the melt, *in-situ* measurements of hydroxide containing ions with an electrochemical analytic system based on cyclic voltammetry (CV) provide unique possibility to monitor impurity concentrations and thus