Electrochemical Method for Monitoring Corrosive Impurities in Molten $MgCl_2$/KCl/NaCl Salts for Thermal Energy Storage

Wenjin Ding[a] (wenjin.ding@dlr.de), Alexander Bonk[a], Joachim Gussone[b], Thomas Bauer[a]

[a]*Institute of Engineering Thermodynamics, German Aerospace Center (DLR), Stuttgart / Cologne, Germany*

[b]*Institute of Materials Research, German Aerospace Center (DLR), Cologne, Germany*

INTRODUCTION

- **Molten chloride salt mixtures** are promising thermal energy storage (TES) materials in **concentrated solar power (CSP)** plants due to physicochemical and thermal properties, e.g., **High thermal stability** (up to 700 °C) for higher efficiency of thermal to electrical energy conversion.
- However, the application of molten chloride salts at higher temperatures causes additional challenges, particularly **increased corrosiveness** of structural materials.

- Corrosion rates significantly depend on concentration of **oxide/hydroxide impurities** in the molten salts [1-3].
- In this work, an electrochemical analysis system based on **cyclic voltammetry (CV)** is being developed to measure the concentration of impurities in molten salts *in-situ* for **corrosion control**.

METHODS

Set-up for CV tests

- Tungsten as working electrode to *in-situ* measure concentration of $MgOH^+$
- Glassy carbon as working electrode for O^{2-}
- Salt sample collector for salt sample collection
- Acid consumption method (AC) for post-analysis of impurities concentration in salt samples

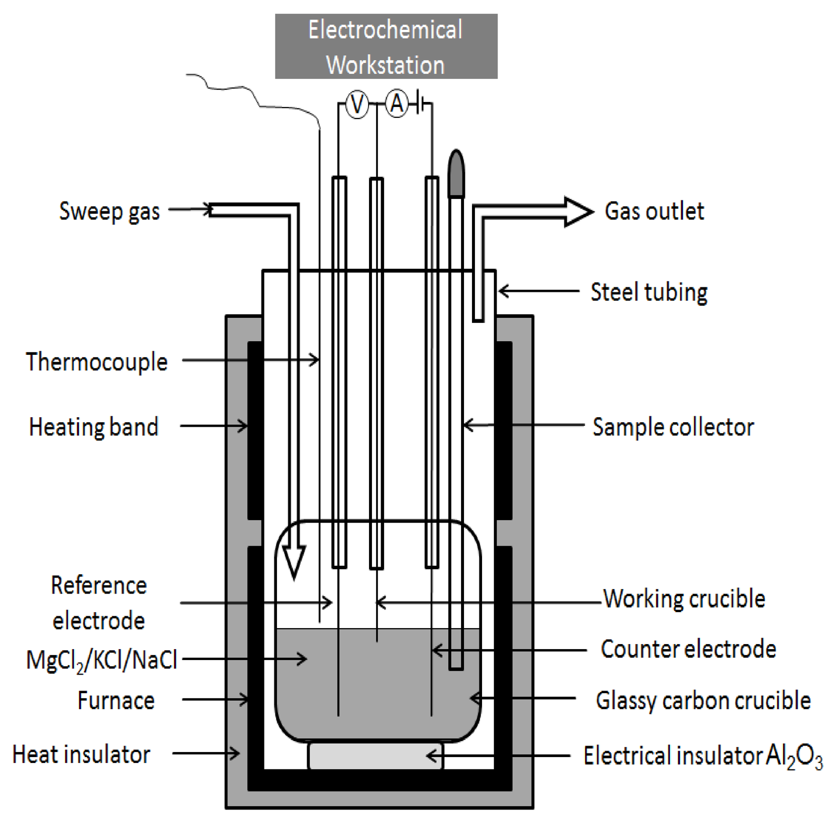

Figure 1: Schematic of experimental set-up for CV experiments on molten salts $MgCl_2$/KCl/NaCl (60/20/20 mole%). Counter and reference electrodes are both tungsten.

Cyclic voltammetry (CV)

- Electrochemical reactions in Figure 2 [4]:
  - A: $Mg^{2+} + 2e^- = Mg$
  - A': $Mg = Mg^{2+} + 2e^-$
  - B: $MgOH^+ + e^- = MgO + ½ H_2$
  - C: $Cl^- = ½ Cl_2 + e^-$
- Relation between peak current density i_p and bulk concentration c^∞ of reactive species, e.g. [4]:

$$i_p(B) = k(T,\nu)\cdot c^\infty(MgOH^+)$$

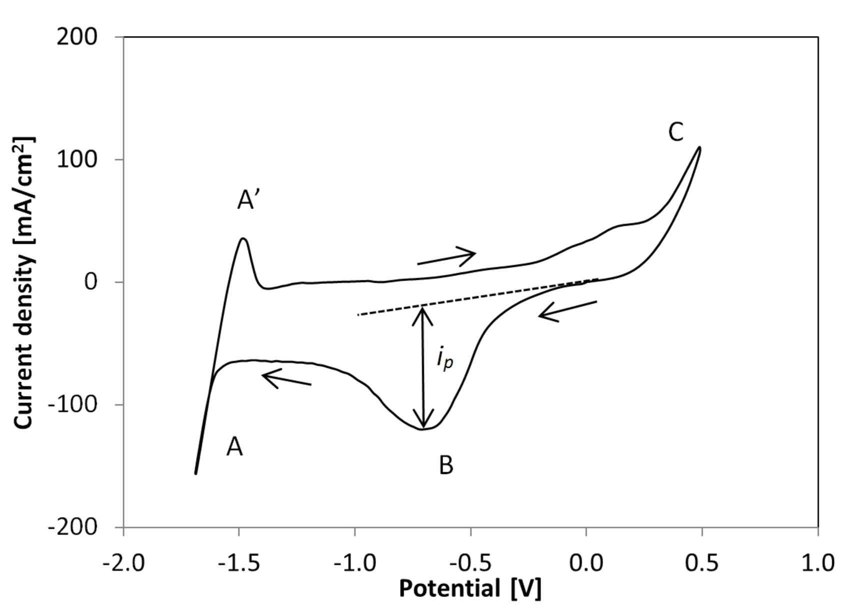

Figure 2: Cyclic voltammogram obtained on a tungsten electrode in the eutectic $MgCl_2$/KCl/NaCl at 500 °C. Sweep rate v: 200 mV/s. Counter and reference electrodes are both tungsten.

$k(T,\nu)$: Constant as a function of temperature T and sweep rate v.

RESULTS

Pre-electrolysis (PE)

- Direct current PE
- Voltage between the working and counter electrode = –2V
- Remove of the noise in cyclic voltammograms caused by unknown impurities

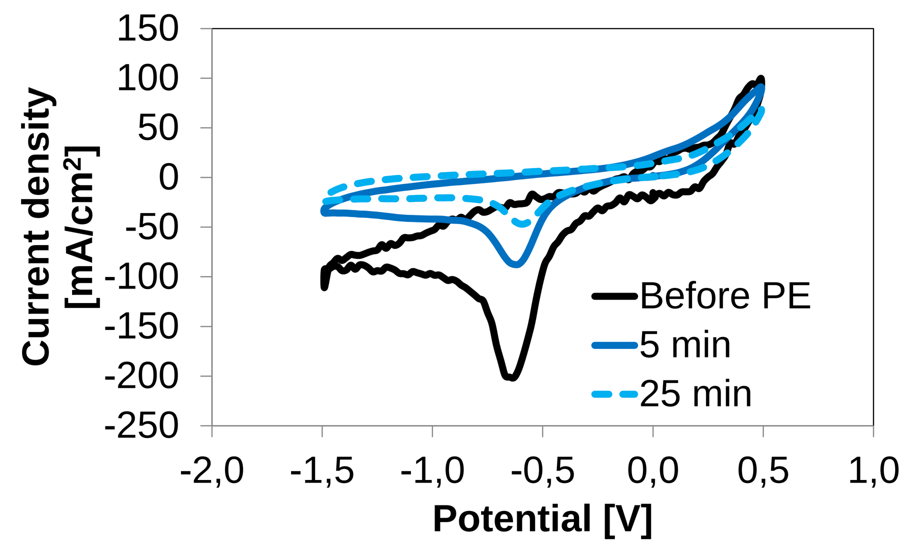

Figure 3: Cyclic voltammograms of molten salts before and after direct current pre-electrolysis at 500 °C. Working, counter and reference electrodes are tungsten. Sweep rate: 200 mV/s.

Determination of $k(T,\nu)$ from PE data

- Fitting concentrations of $MgOH^+$ from CV with those from AC *via* the least-square method:

$$\sum_{i=1}^{n}\left(c_i^{CV}(k)-c_i^{AC}\right)^2 = \text{minimal}$$

- $k(T,\nu)$ = 1.8±0.6 A m/mol

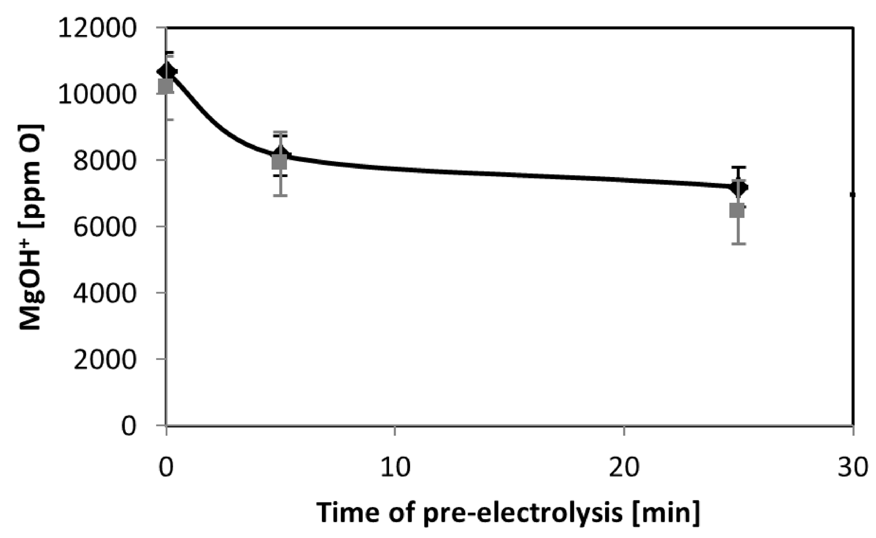

Figure 4: Concentrations of corrosive impurity $MgOH^+$ in molten salt over the time of PE determined with the CV (black curve) and acid consumption (grey points) method, respectively.

CV experiments after adding NaOH

- Confirmation of Peak B for $MgOH^+$: a significant change of peak B was observed after adding NaOH.
- The concentrations of $MgOH^+$ determined from AC compare well with those from the CV experiments, when the determined constant $k(T,\nu)$ from PE was used in the calculation.

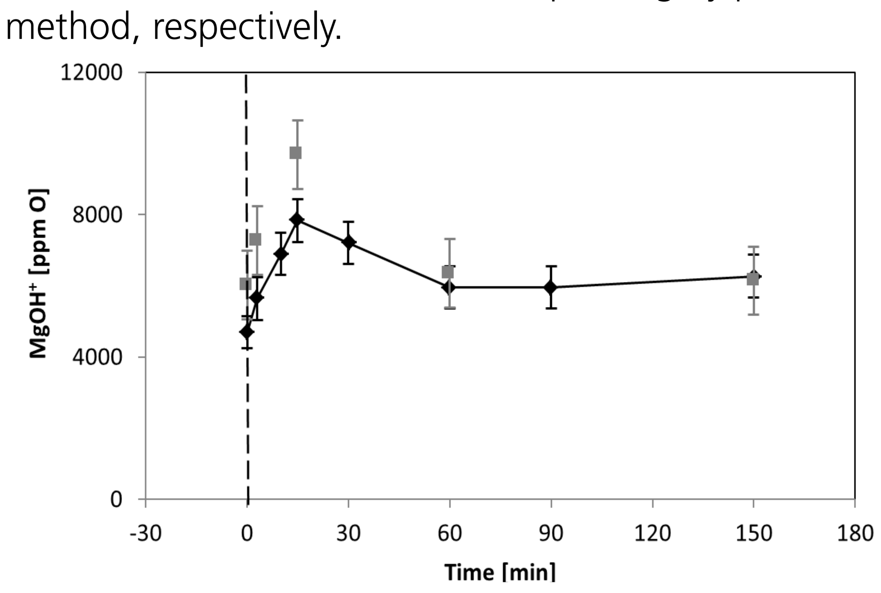

Figure 5: Concentration of $MgOH^+$ (black points and curve: CV data; Grey points: AC data) as a function of time after adding 4286 ppm O NaOH.

CONCLUSIONS & APPLICABILITY

This work presented the successful commissioning of an experimental set-up to study molten chloride melts *in-situ* (by CV) and *ex-situ* (post-analysis of salt samples by AC). Correlation between both methods could be established. This will allow for further studies of the molten chloride salt chemistry (e.g., corrosion) and development of the process technology for thermal energy storage systems up to 700 °C in the future.

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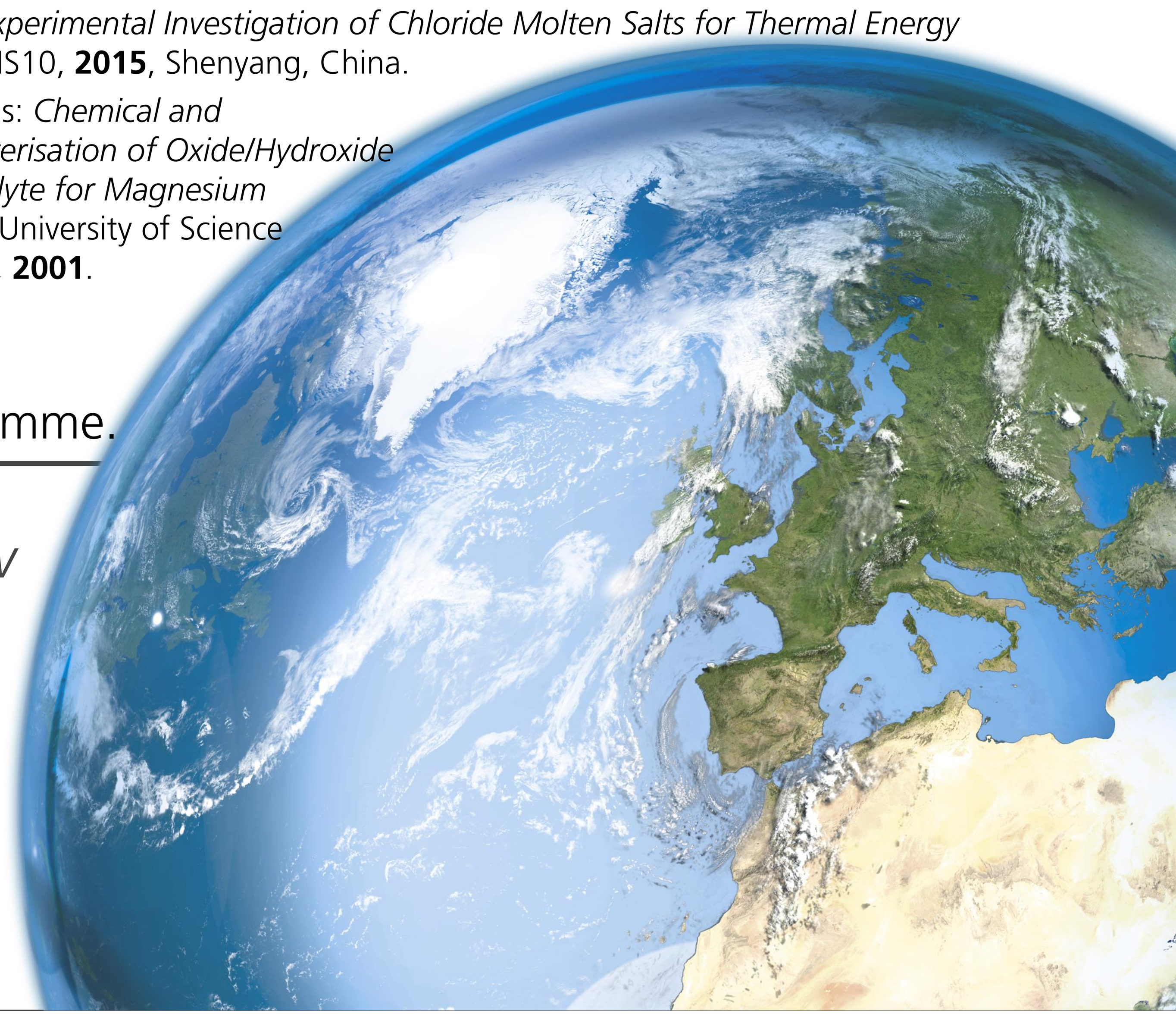

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