## **Accepted Manuscript**

Title: Electrochemical Studies of Molten Sulfates in

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PII: S0010-938X(16)31298-7

DOI: https://doi.org/10.1016/j.corsci.2017.12.022

Reference: CS 7298

To appear in:

Received date: 9-12-2016 Revised date: 13-12-2017 Accepted date: 18-12-2017

Please cite this article as: Kuldeep Kumar, Nathan D.Smith, Timothy Lichtenstein, Hojong Kim, Electrochemical Studies of Molten Sulfates in LiCl-KCl-Na2SO4 at 700x202f;deg;C, Corrosion Science https://doi.org/10.1016/j.corsci.2017.12.022

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Electrochemical Studies of Molten Sulfates in LiCl-KCl-Na<sub>2</sub>SO<sub>4</sub> at 700 °C

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**Highlights:** 

 $SO_4^{2-}$  is electrochemically reduced to S and  $S^{2-}$ , only at large overpotentials.

SO<sub>4</sub><sup>2-</sup> reduction reaction is irreversible with slow charge transfer kinetics.

Oxidizing O<sub>2</sub>-SO<sub>2</sub> atmosphere drastically shifts OCP in the positive direction.

Gas atmosphere and thermal stability affect reduction reactions in molten sulfates.

**ABSTRACT** 

The electrochemical reduction behavior of molten Na<sub>2</sub>SO<sub>4</sub> was investigated at 700 °C in LiCl-

KCl-Na<sub>2</sub>SO<sub>4</sub> (5–15 mol%) electrolyte under two different gaseous atmospheres of inert argon and

oxidizing O<sub>2</sub>-0.1% SO<sub>2</sub>. Sulfate ions (SO<sub>4</sub><sup>2-</sup>) were directly reduced into sulfur (S) and sulfide (S<sup>2-</sup>

) ions at large negative overpotentials in both gaseous atmospheres. During the transition from

inert to oxidizing atmosphere, open circuit potentials of a platinum electrode (vs. Ag/Ag<sup>+</sup>) were

shifted in the positive direction by more than 0.60 V, implying the presence of stronger oxidants

which can be coupled with the metal oxidation reactions during the hot corrosion processes.

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