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Cathodic Reduction Kinetics on Stainless Steel Surfaces in Corrosive Low Humidity Environments

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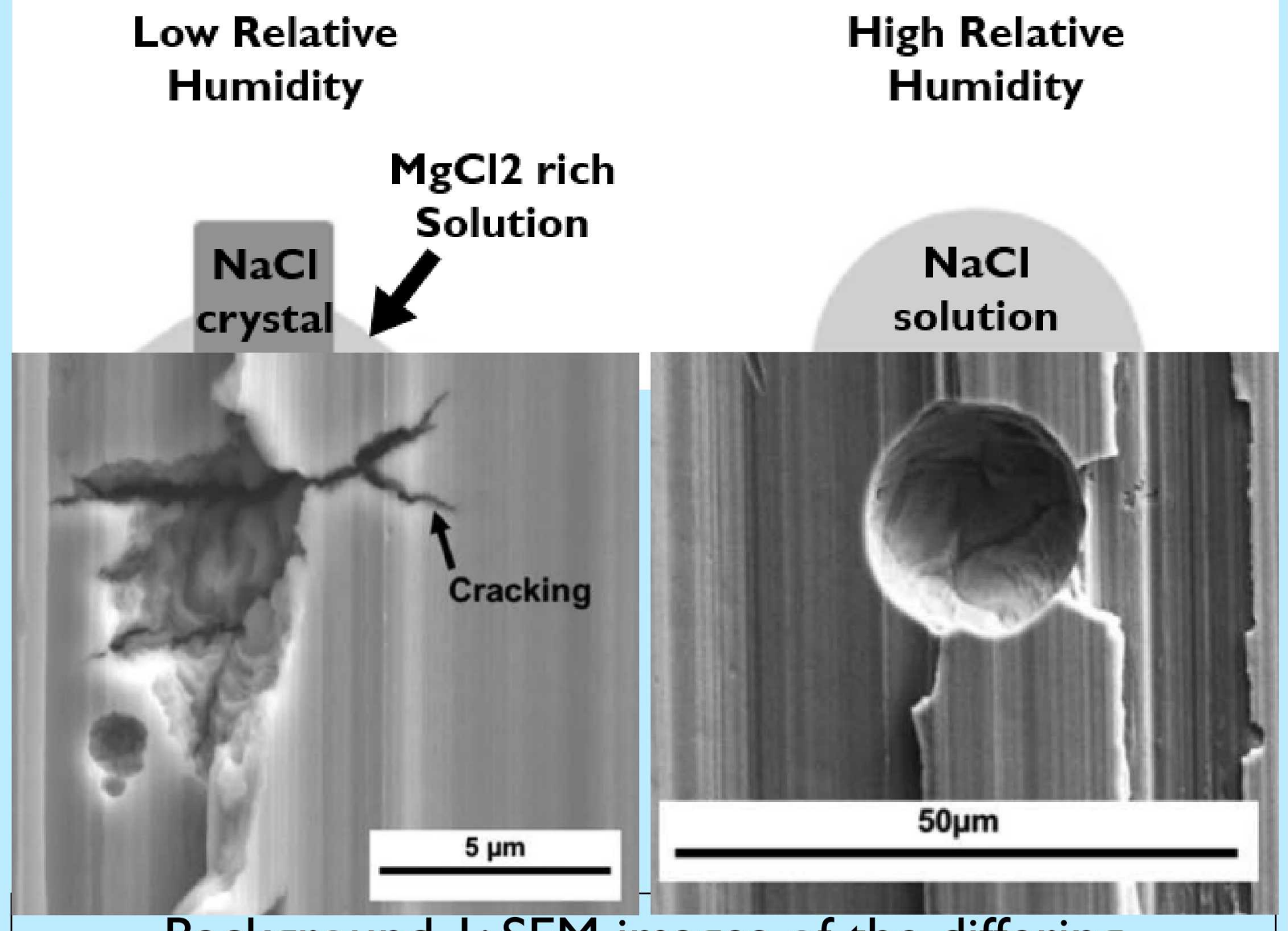
Motivation

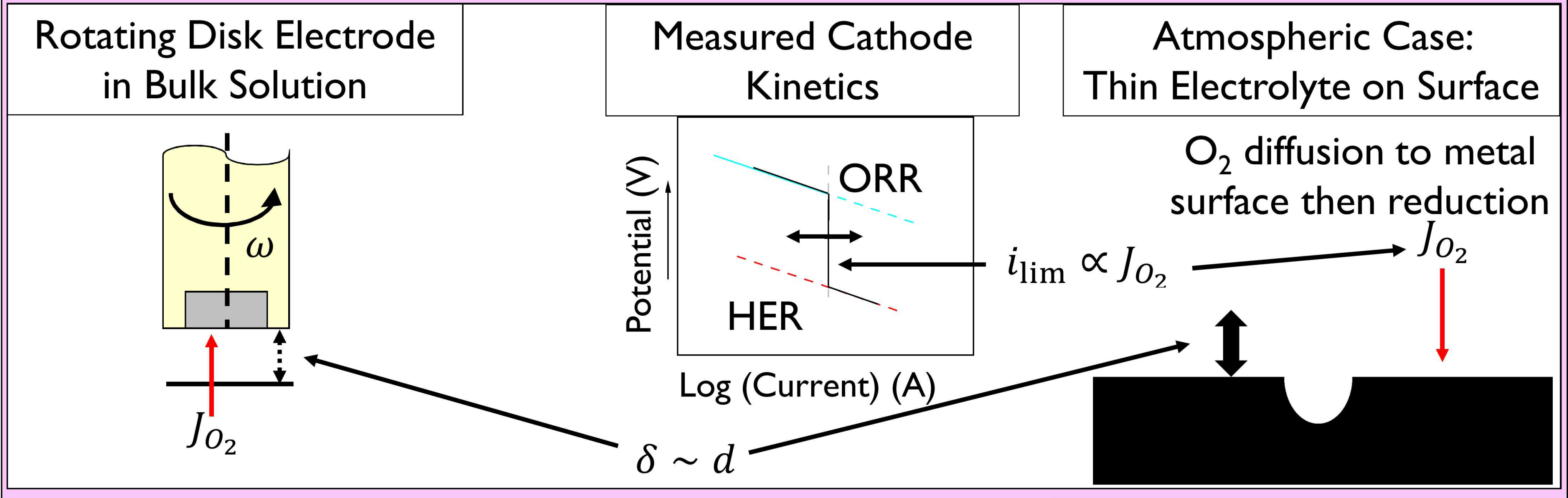
- Corrosion is a multibillion dollar cost annually.
- Seaside environments are particularly corrosive to metals and alloys due to the deposition of corrosive atmospheric seawater water aerosols.
- Relative humidity controls the physicochemical nature of the brines that form from the wetted particles and, in turn, corrosion mechanisms.
- The specific underlying electrochemical processes that drive corrosion and its humidity-dependence is not well understood. This knowledge gap inhibits development of reliable corrosion damage models for lifetime prediction.
- Electrochemical cathode kinetics are the driving force for atmospheric corrosion and good starting point for developing predictive models.
- The primary reaction for cathodic processes are oxygen reduction reaction (ORR)($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$) and hydrogen evolution reaction (HER) ($2H_2O + 4e^- \rightarrow 2OH^- + H_2$) and will be of the utmost importance in this study.



Background 1: SEM images of the differing morphologies of corrosion pits formed under sea salt particles at low (left) and high (right) humidity. Stress corrosion cracking (SCC), cracks resulting from both corrosion and mechanical stress, is much more common in low humidity environments and causes premature unpredictable failure.

<u>This study focuses on low humidity cathode kinetics to learn about pit propagation and Stress Corrosion Cracking in 304L Stainless Steel</u>

Experimental Approach



Rotating Disk Electrode in Bulk Solution

Measured Cathode Kinetics

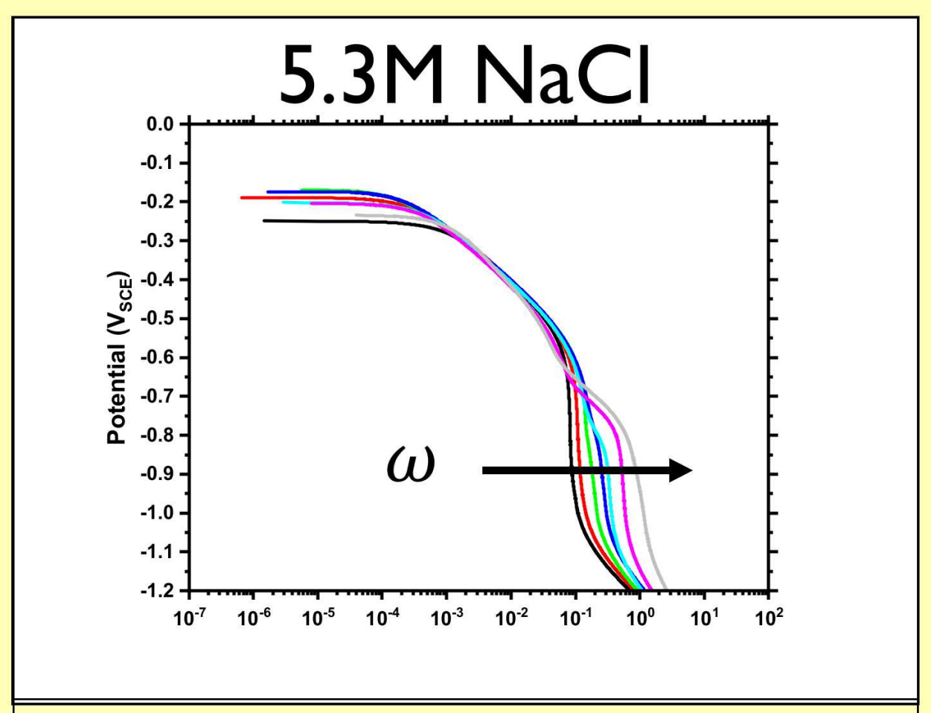
Atmospheric Case: Thin Electrolyte on Surface

- A rotating disk electrode (RDE) immersed in aqueous magnesium chloride solutions of varying concentration was used to measure the cathode kinetics that drive metal corrosion.
- Electrode rotation speed simulates the effect of different thicknesses of microscopic brine layers on atmospheric surfaces

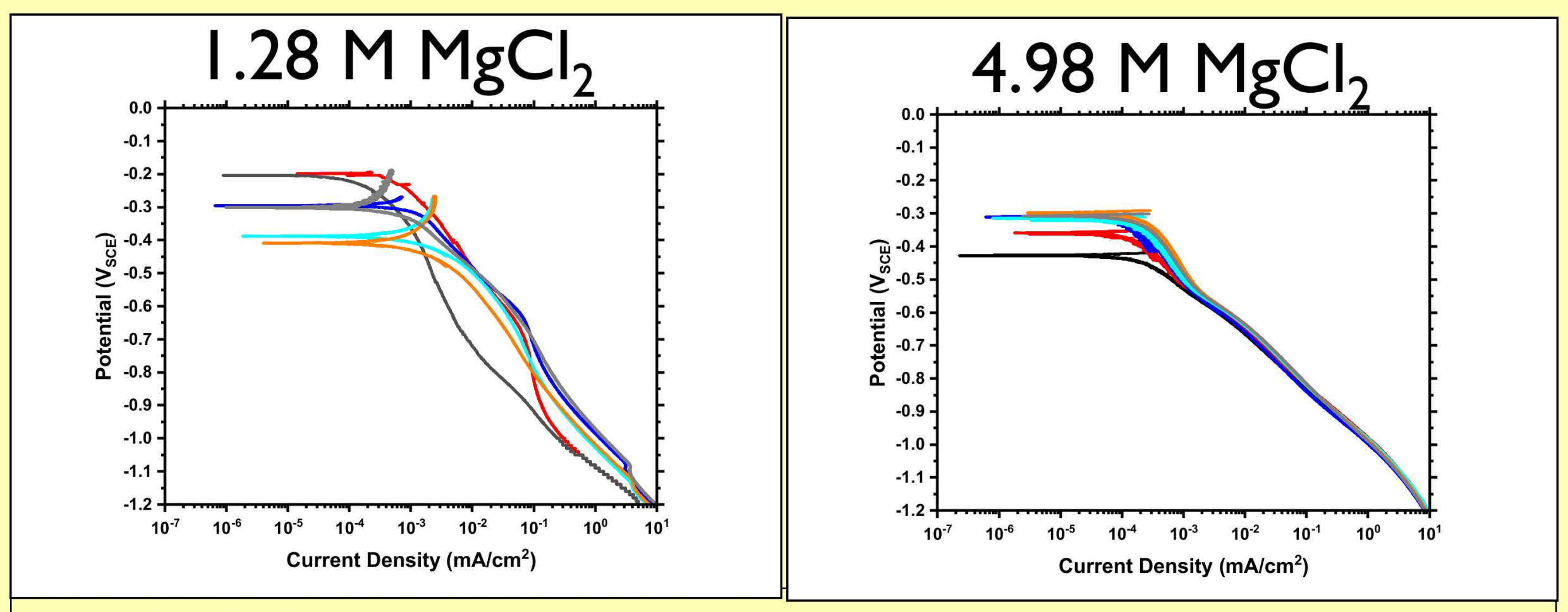
<u>Terms (from left to right)</u>

J_{O_2}=Oxygen flux through boundary
δ=Boundary thickness on RDE
ω=RDE angular frequency
d = electrolyte thickness in the real system.
i_{lim}=Mass transfer limited current

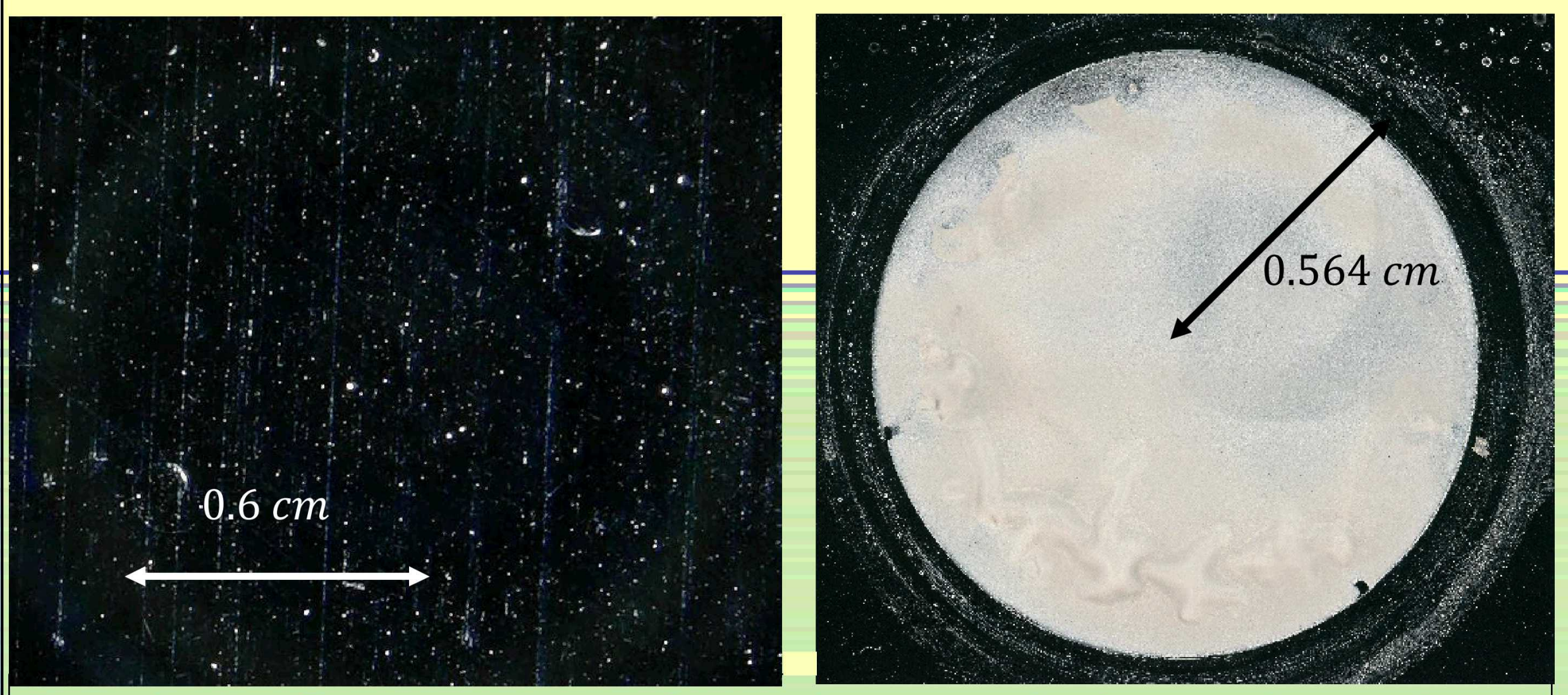
Results



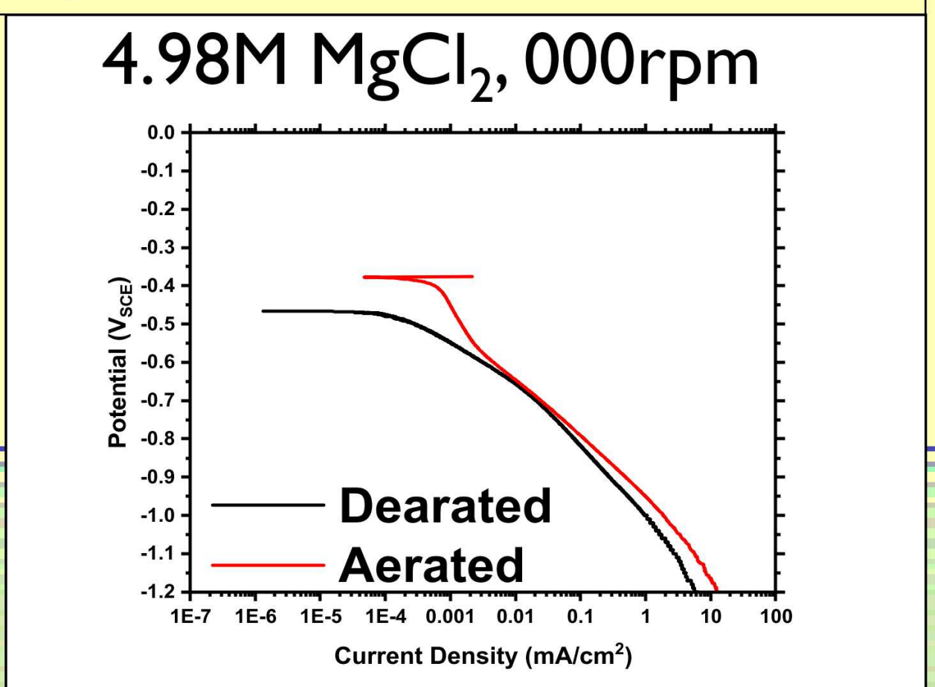
<u>Result 1:</u> Polarization measurement in high RH environment shows oxygen reduction reaction (ORR) is dominant.



<u>Result 2:</u> Polarization curves across a variety of rotation speeds and $MgCl_2$ concentrations. There is no trend with rotation speed. Instead of ORR, Hydrogen Evolution Reaction (HER) is shown as the dominant reaction at both concentrations, in all rotation speeds.



Result 4: Comparison of stainless steel electrode surfaces after a cathodic polarization experiment. There is a film adhered to the surface that may contain precipitated magnesium salts. It is not known whether the film deposited directly onto the surface or if the species precipitated in the mass transfer boundary layer near the surface and became adhered after removal from the cell.



<u>Result 3:</u> Two Polarization curves showing the behavior of the system in saturated oxygen vs saturated nitrogen. Saturating with nitrogen removes most of the oxygen from the system, testing the dependence on oxygen concentration. This further confirms the observation from Result 2 that HER is the dominant cathodic Reaction.

Discussion

The most important result from this study is the different dominant reaction in low humidity, magnesium chloride rich environments. This discussion aims to (1) connect the kinetics (Result 2) to the film observed in Result 4 and (2) determine the cause of the current density behaviors shown in Result 2. Because both dominant cathode reactions produce hydroxide ions, any non-zero current from these two reactions causes the pH close to the surface of the electrode to rise far above the bulk value.

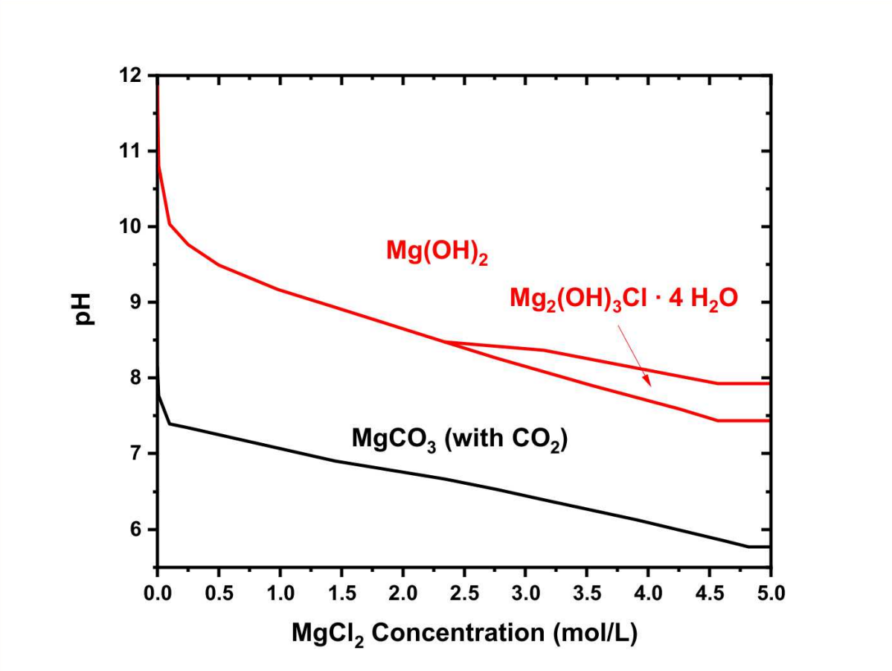


Figure 1: A Speciation diagram calculated with EQ3/6 thermodynamic modeling software. When the cathode reactions cause the pH to rise, this speciation diagram shows that the solution will precipitate magnesium salts. The Mg^{2+} ions will buffer the pH to a particular precipitation pH and prevent further change. According to the diagram, the pH is buffered to values far lower than in high RH systems. Any new hydroxyl ions will be incorporated into the precipitate film.

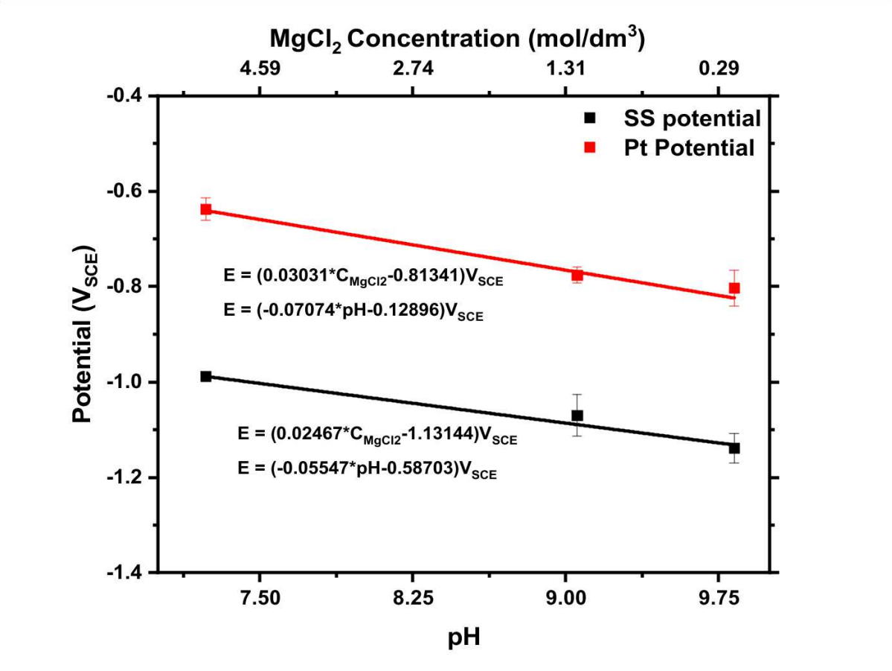


Figure 2: Potentials at which the current is 1mA/cm^2. The pH axis was calculated using the $Mg(OH)_2$ line from Figure 1, but the trend holds using the $MgCO_3$ line as well. 1mA/cm^2 is high enough that for all potentials at this current, HER is the dominant reaction. Therefore, changes in this value can tell us about the behavior of HER and its relationship with pH. The potential is shown to change as ~60mV/pH which fits with previously proved literature for HER (I.E. The Nernst Equation).

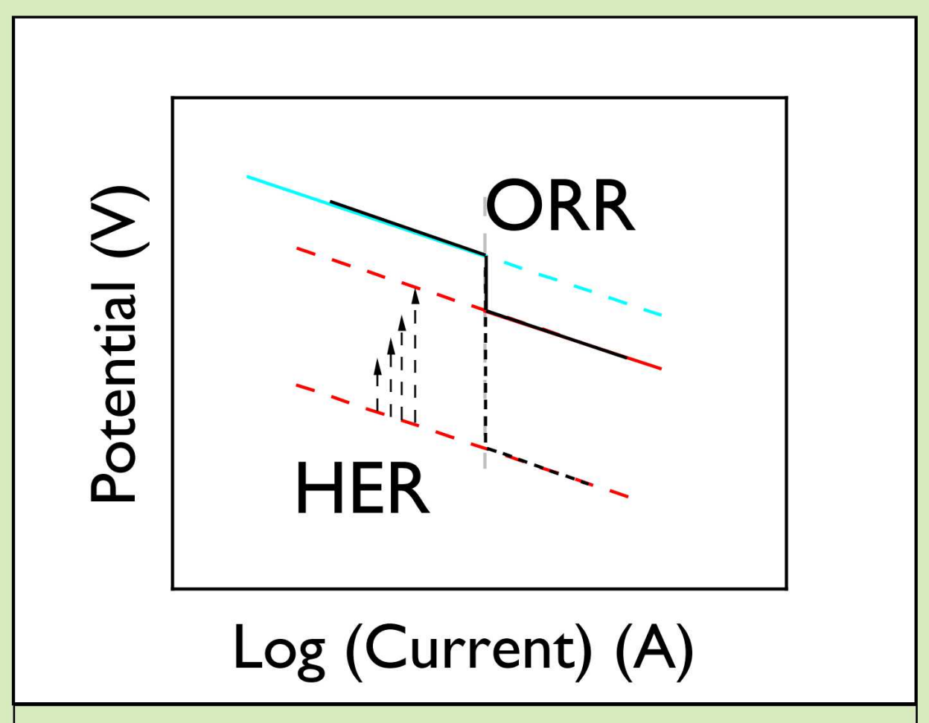


Figure 3: Theoretical polarization curve showing how HER would change if the pH was buffered to a value much lower than similar systems. When the pH is lowered, the potential at which HER starts becomes more positive. This causes HER to overtake ORR and become the dominant reaction in the system.

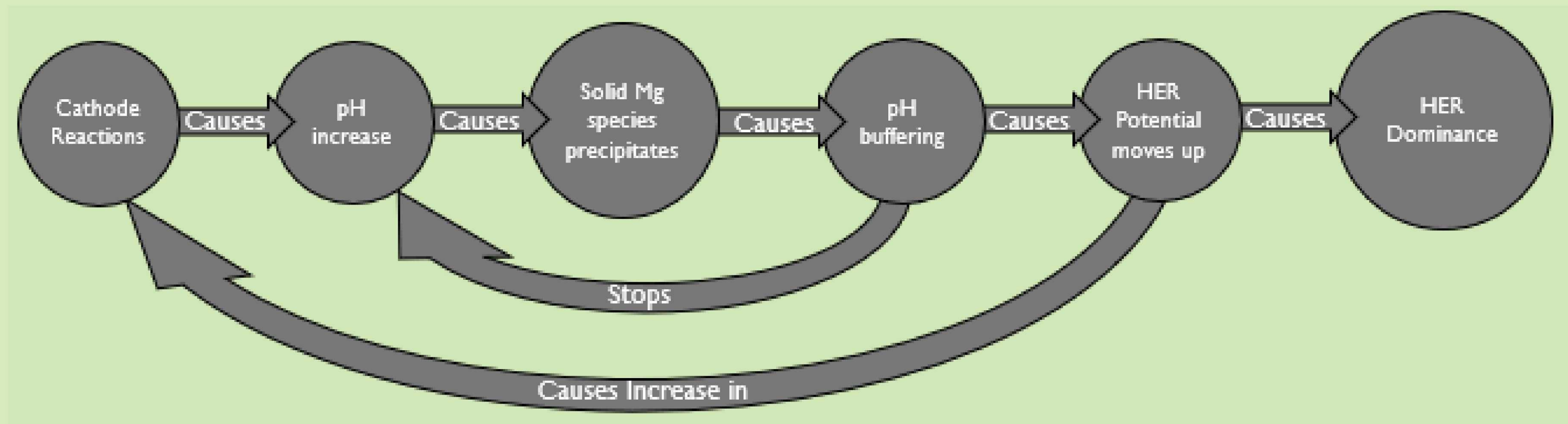
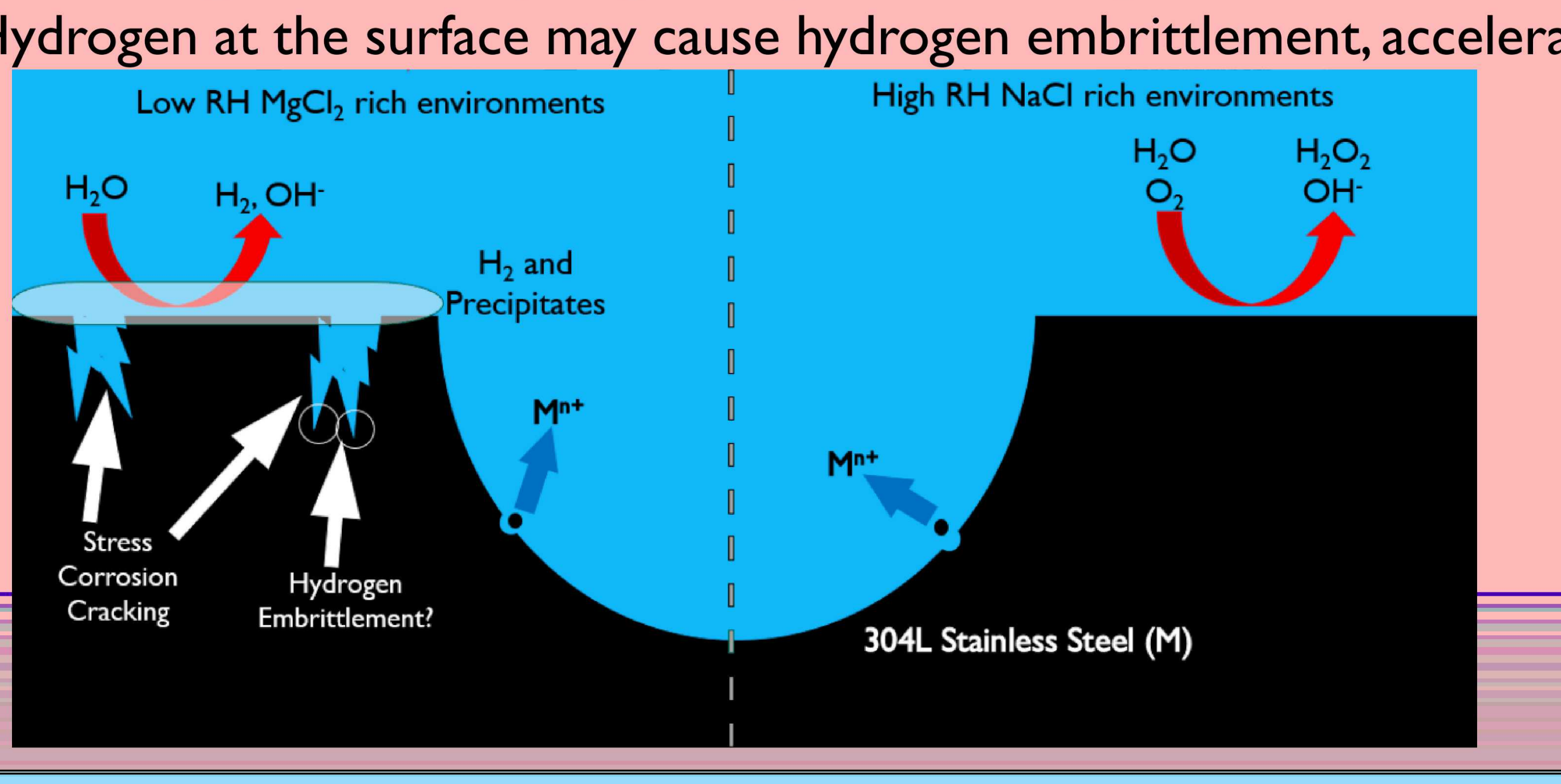


Figure 4: Summarizes the processes that contribute to HER becoming the dominant reaction in low RH environments.

Conclusions and Implications

1. In concentrated $MgCl_2$ brines, representative of low humidity seawater environments, on 304L SS, hydrogen evolution replaces oxygen reduction as the dominant cathode reaction.
2. Hydrogen Evolution is the dominant cathodic reaction on 304L stainless steel surfaces because of Mg^{2+} ion buffering the solution to lower pHs
3. This creates an excess of H_2 at the electrode surface, and due to low diffusion coefficients through salts, the hydrogen may be contacting the surface for even longer
4. Excess Hydrogen at the surface may cause hydrogen embrittlement, accelerating SCC



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EQ 3/6 Software citation

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