

Aluminium Electrochemistry in Electrocoagulation Reactors

Martin Mechelhoff

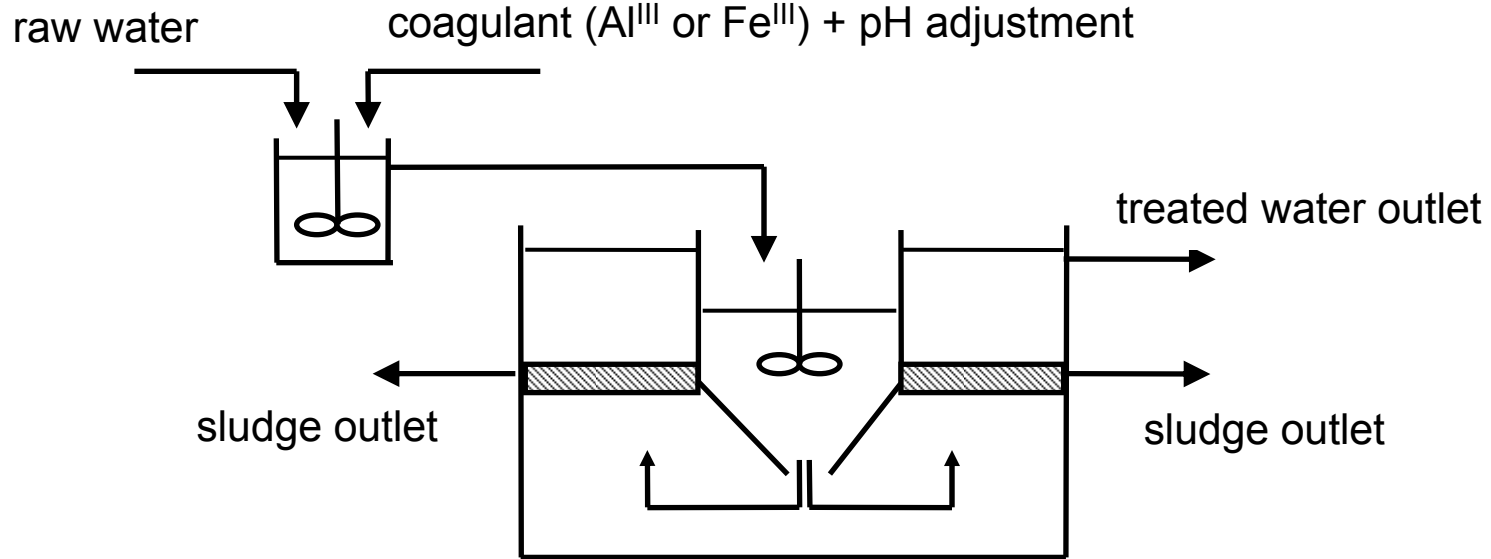
Imperial College London

Department of Chemical Engineering

London SW7 2AZ (UK)

213th ECS Meeting, Phoenix, 18th – 23th May 2008

Conventional Coagulation



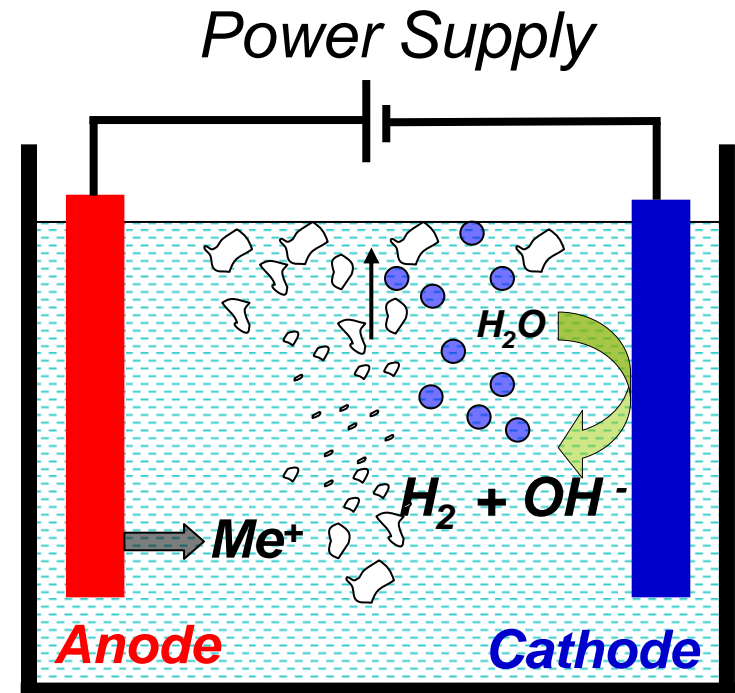
- **Advantage:** well known process
- **Disadvantages:** large footprint
large amounts of liquid chemicals
performance exhausted

Electrocoagulation Reactors

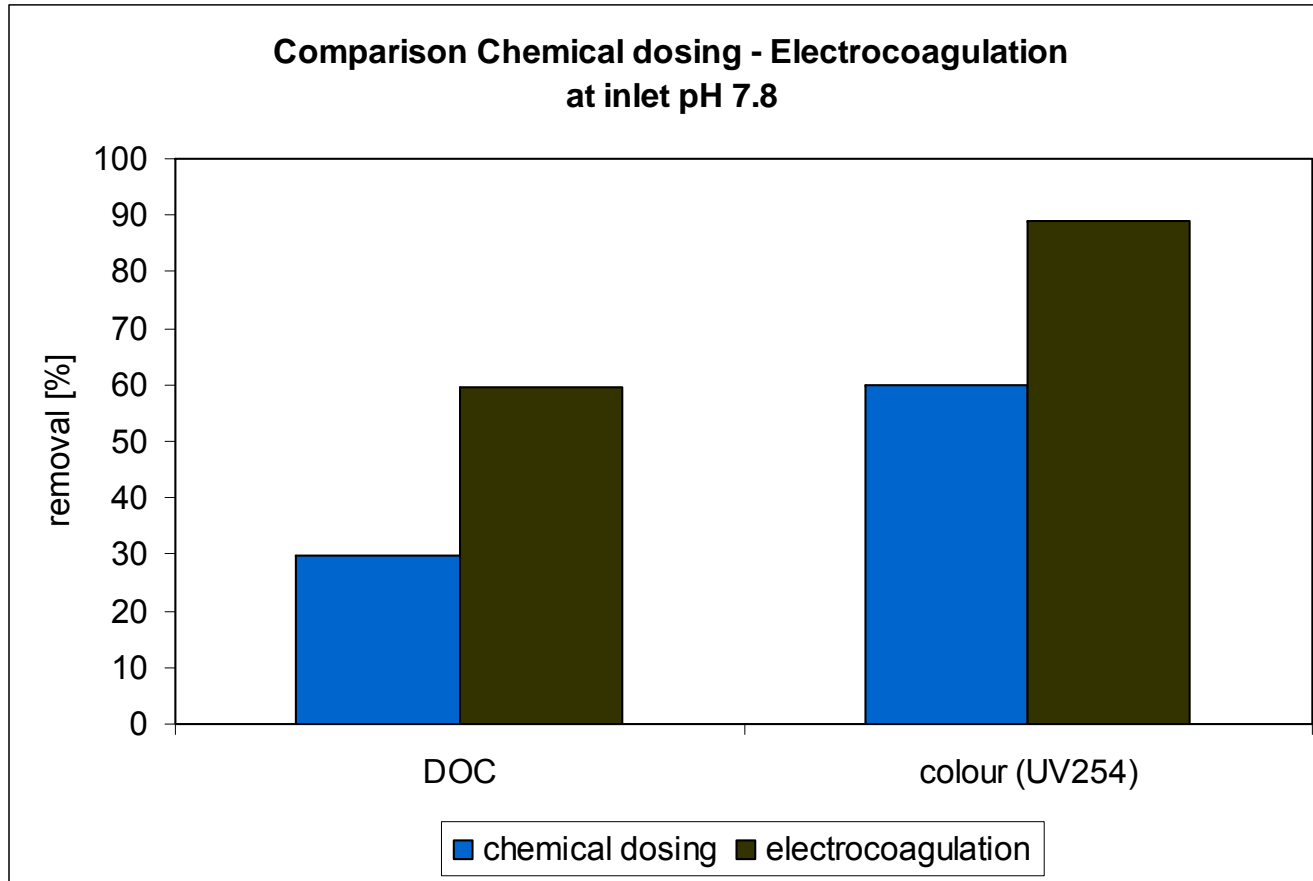
- Water for purification passed through electrochemical reactor
- Anode usually Fe or Al; cathode often steel
- Inter-electrode gap: < 5 mm
- Dissolution, hydrolysis and precipitation of metal ions from electrode
- Simultaneous evolution of H_2 gas
- Destabilisation of suspension \rightarrow coagulation

Main advantage:

No addition of chemicals



Performance and Challenges



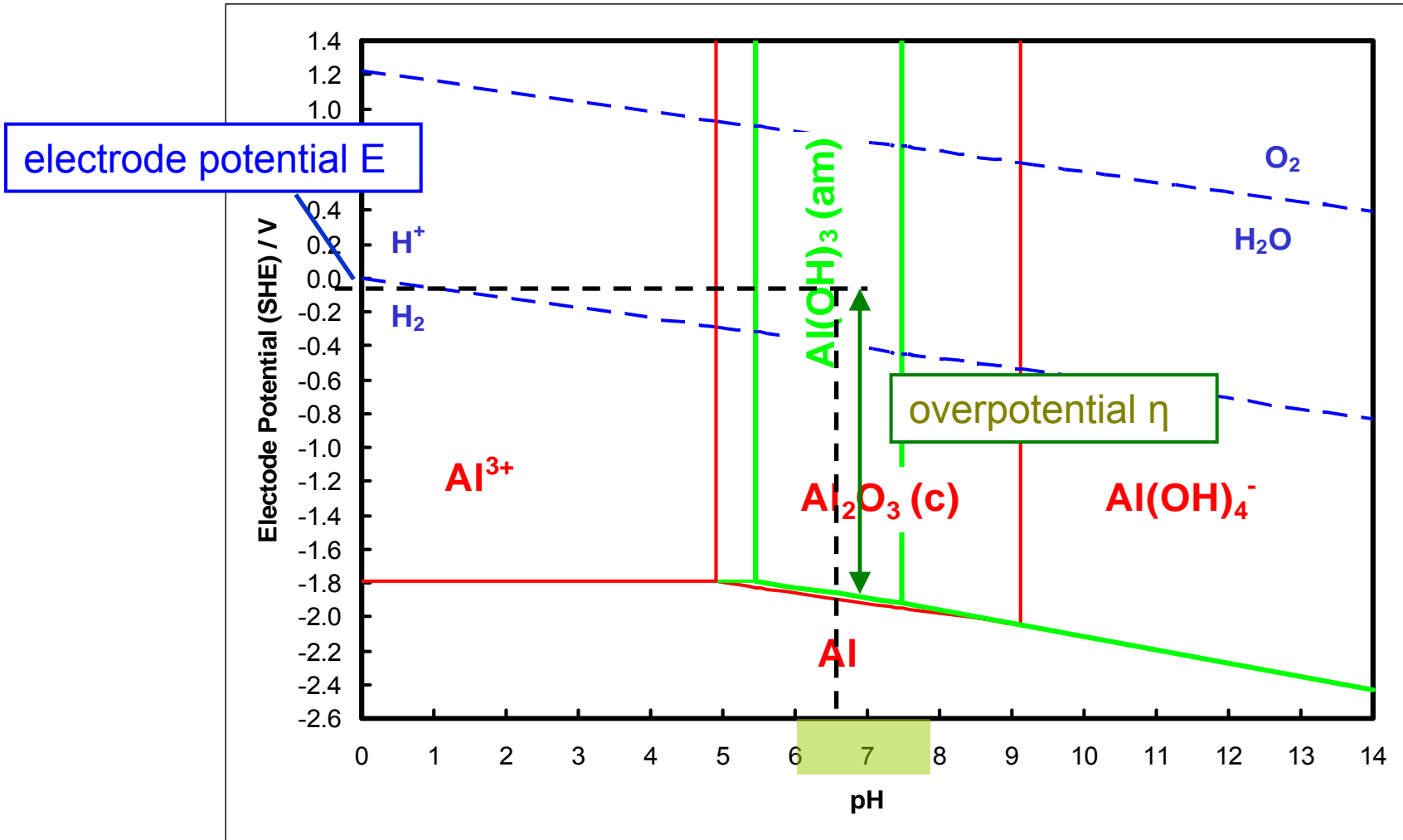
Jiang, J.Q.; Graham, N. et al. (2002); Water Research, 36, 4064-4078

But:

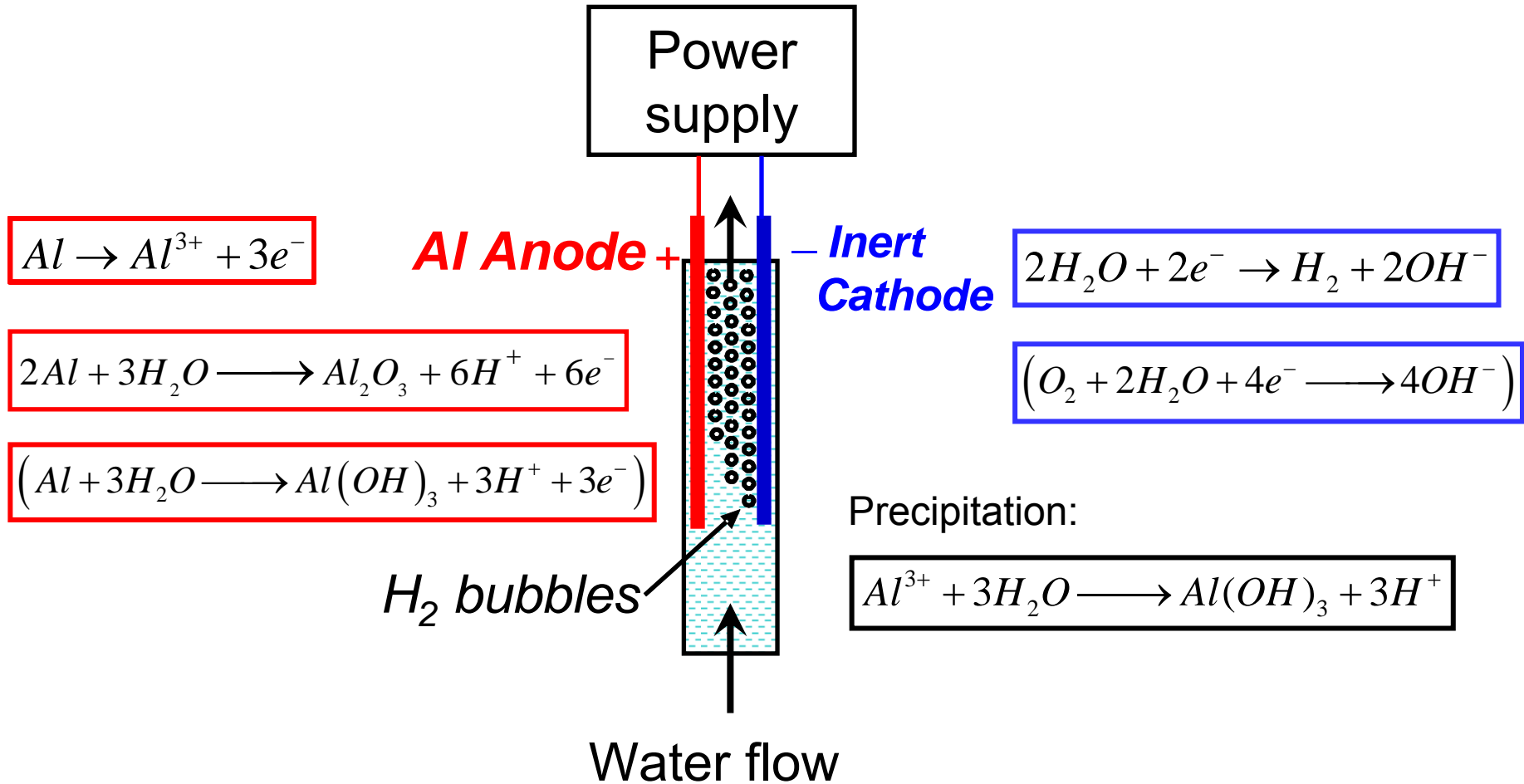
- High cell voltages, thus high specific energy consumption
- Electrode passivation → slow reaction rates

Potential-pH diagram for $Al-H_2O$ system

for 10^{-6} M $Al(III)$ activity at 298 K

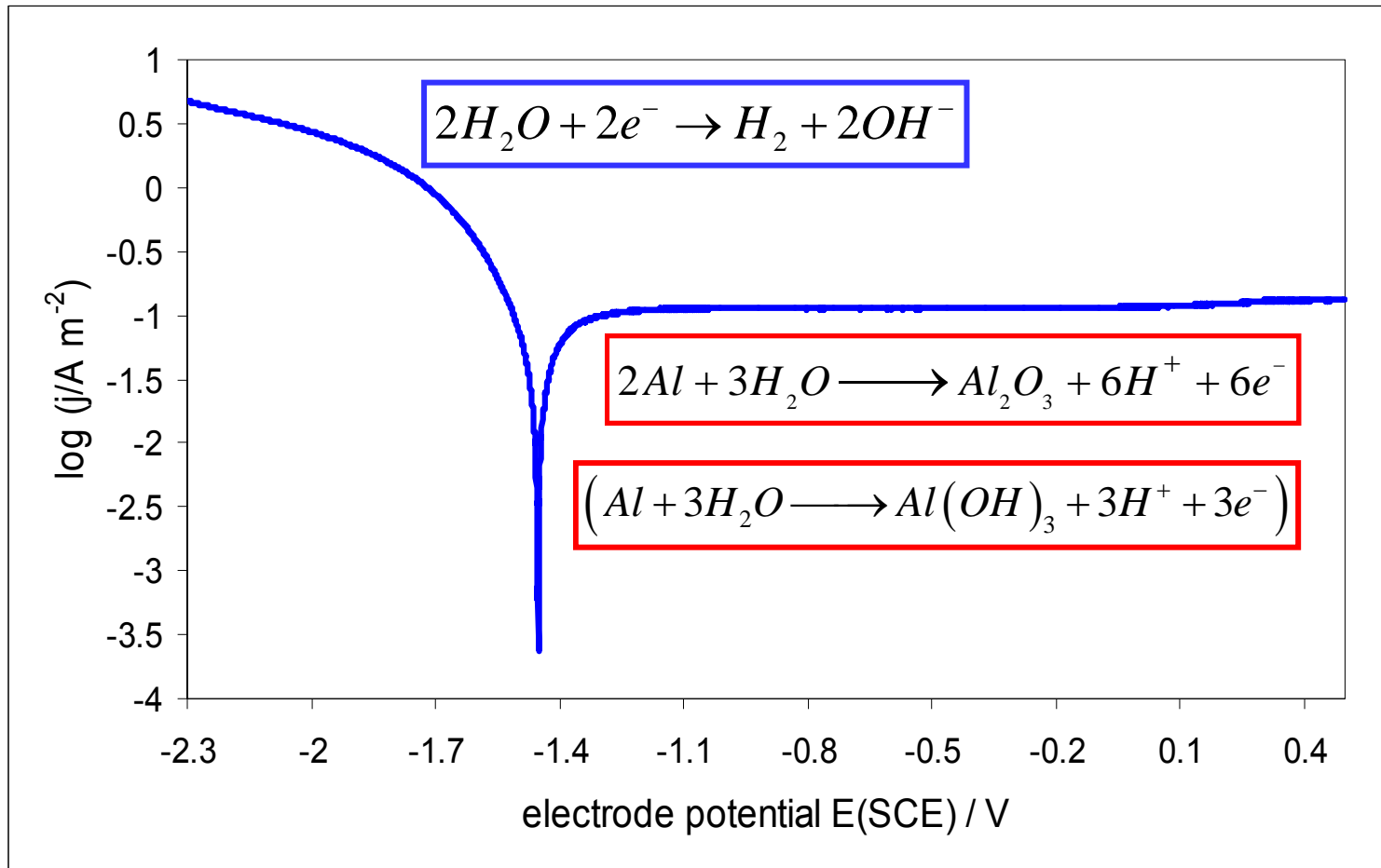


Electrode Reactions



Voltammetric Behaviour of Al

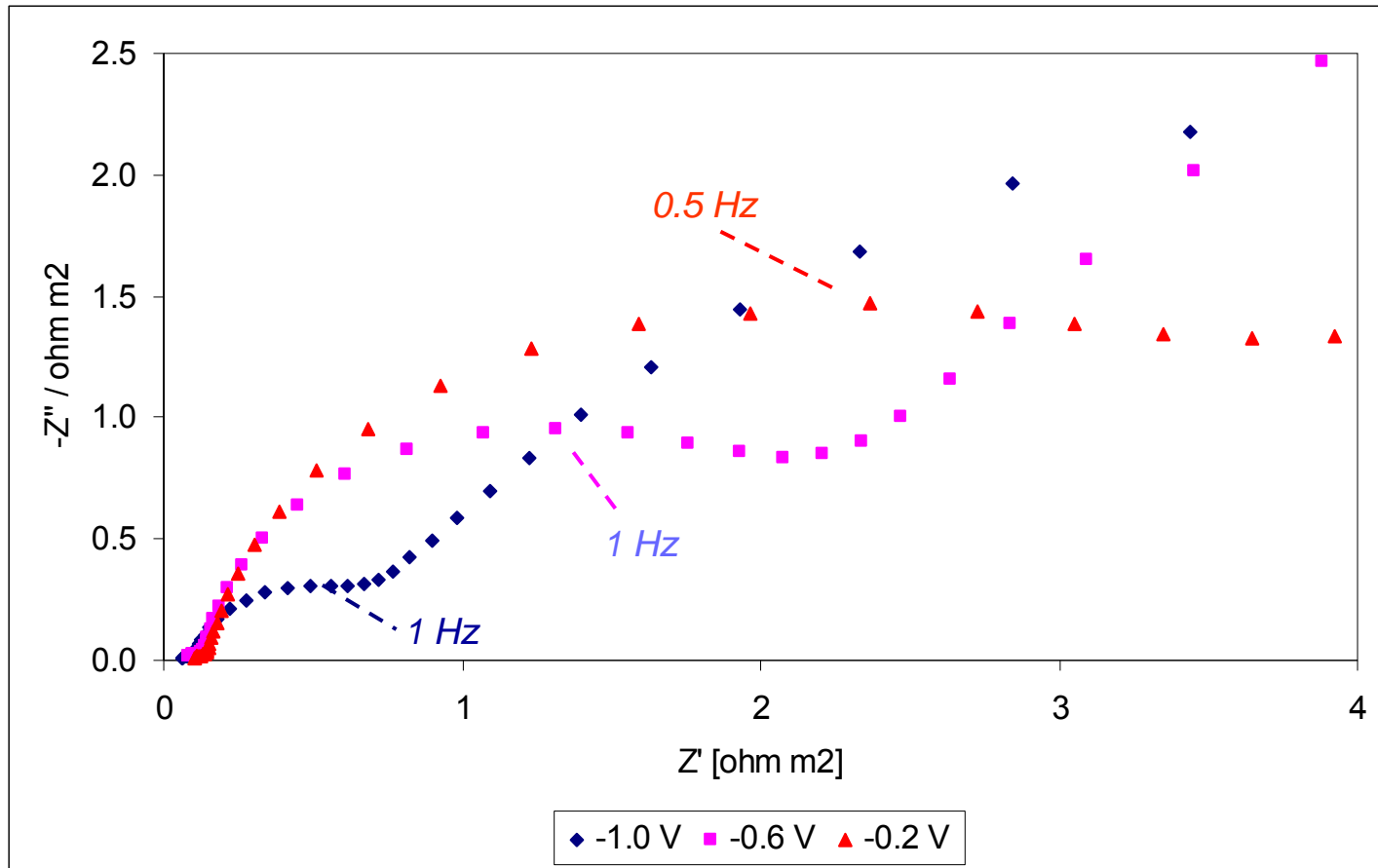
- Passivation impedes dissolution



High purity Al RDE
mirror finish
2000 rpm
 $5 \times 10^{-4} \text{ kmol m}^{-3}$
 Na_2SO_4
 1 mV s^{-1}

Impedance Spectrum

- Three overlapping, slightly depressed semi-circles
- $-Z''(\text{max})$ of second semi-circle increases with growing potential



10^4 – ca. 10^{-2} Hz

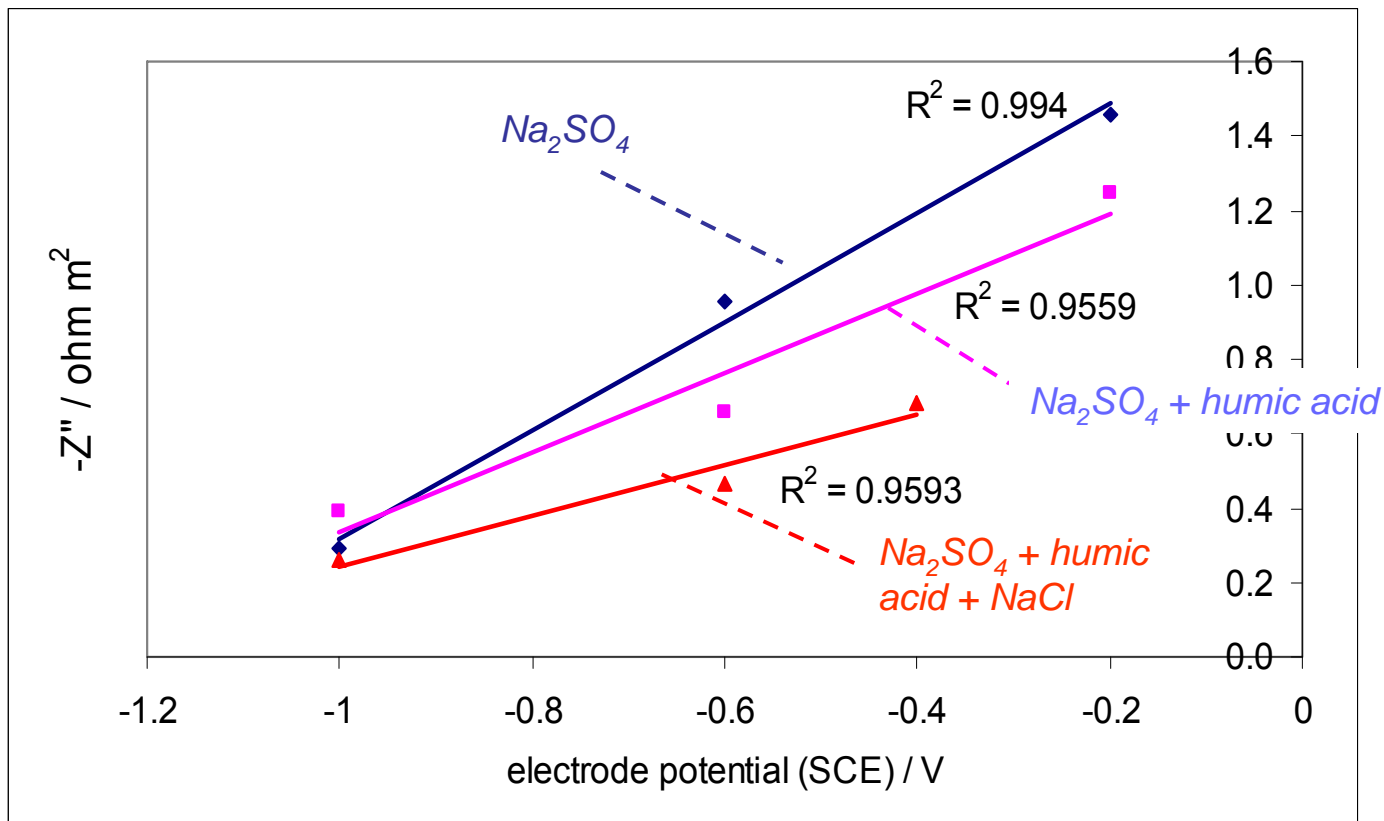
Stationary

Al1050 (99.5%)

5×10^{-4} M Na_2SO_4 +
 10 mg l^{-1} humic acid +
 1.5×10^{-4} mM NaCl

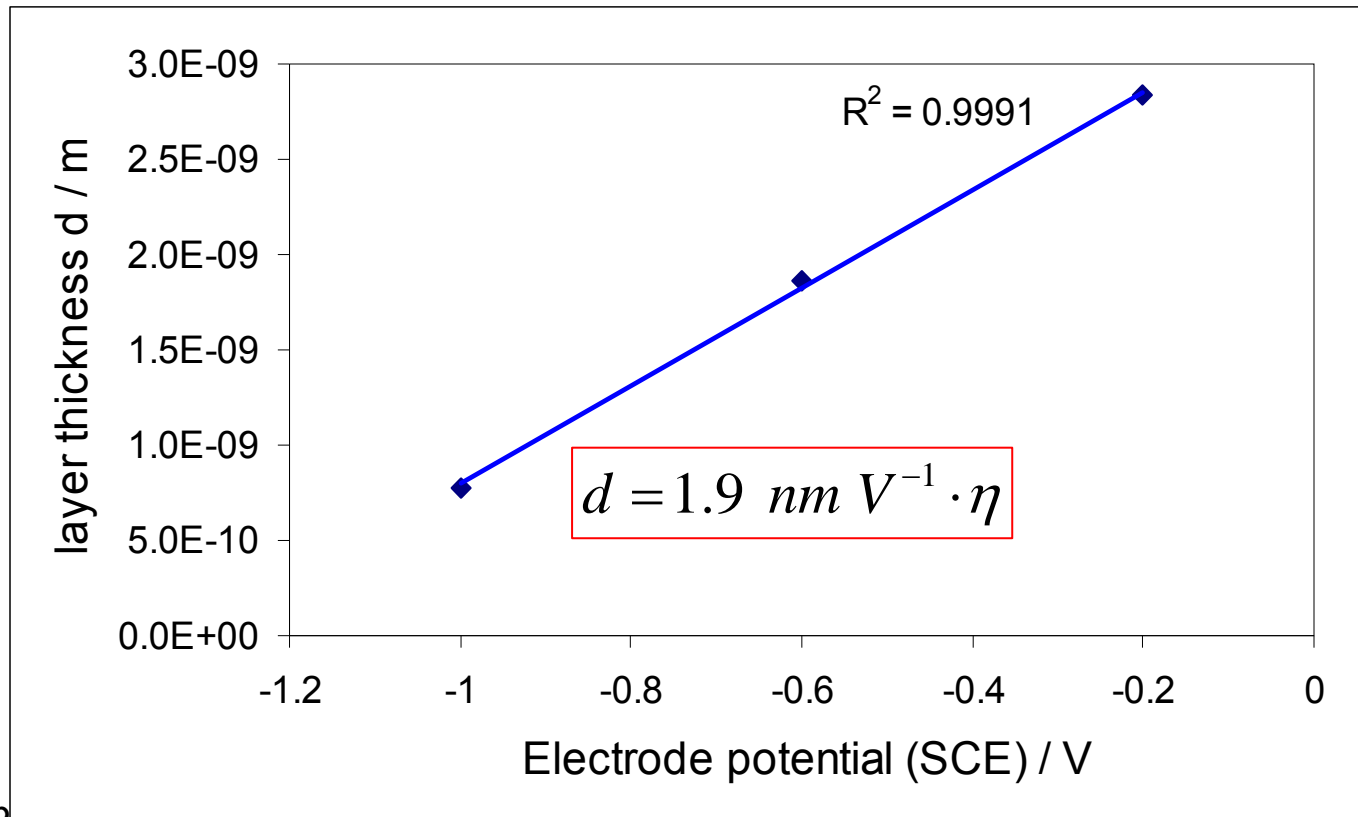
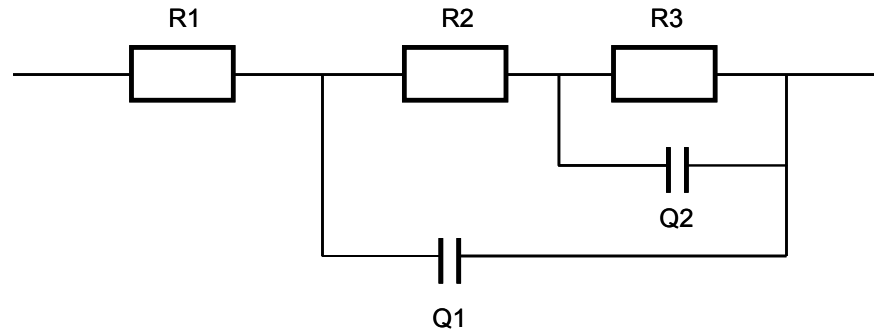
Effect of Potential on Maximum $-Z''$

- $-Z''(\text{max})$ linearly dependent on applied potential
 - Lower values when adding humic acid and NaCl
- interference with surface properties, $\epsilon=?$



Passive Layer Thickness

- Equivalent electrical circuit used for data fitting:



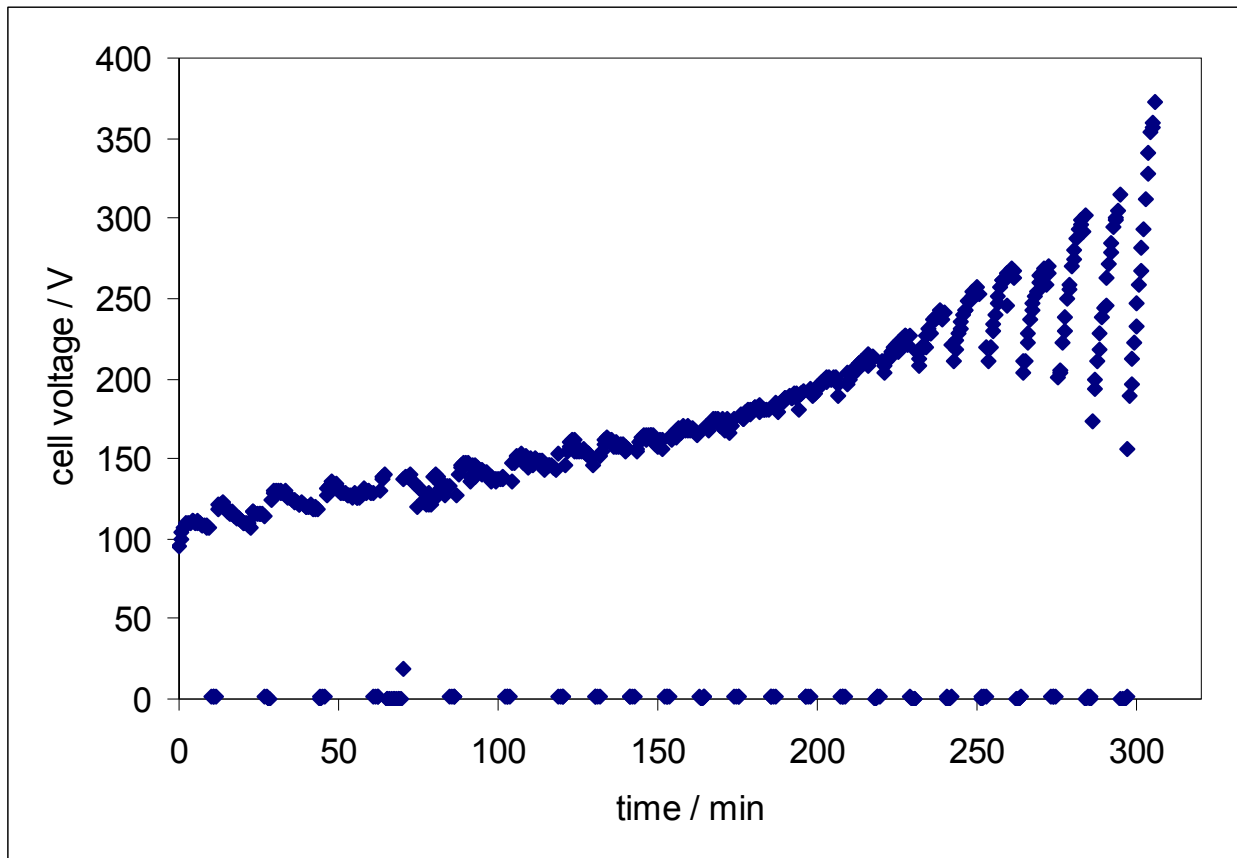
$5 \times 10^{-4} \text{ kmol m}^{-3}$
 Na_2SO_4
With $\epsilon = 9$

Cell Voltage at Constant Current Density

At Yorkshire Water's electrocoagulation pilot plant:

- Constant current density applied: ca. 67 A m^{-2}

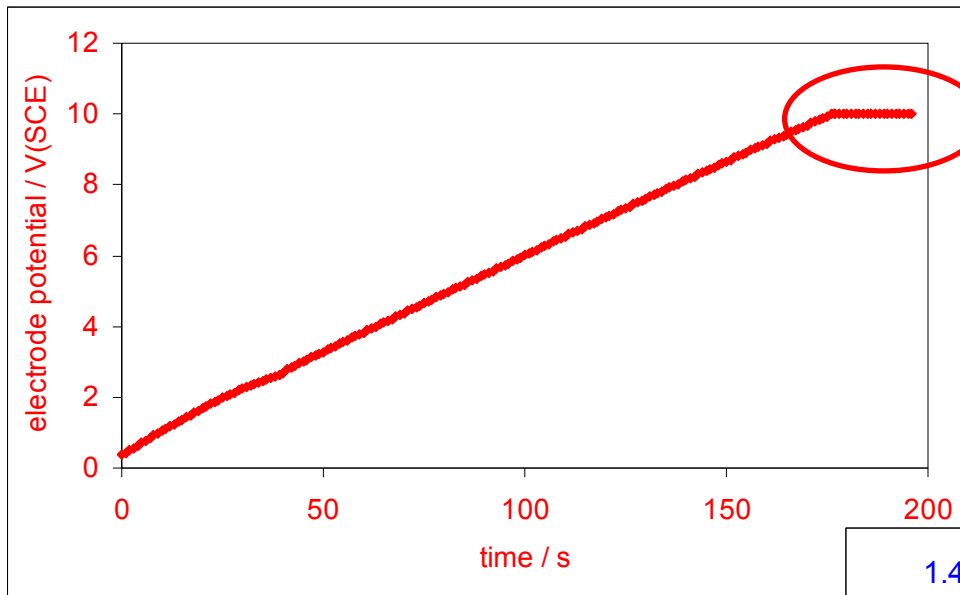
→ Rapid cell voltage increase due to passive layer growth / fouling



Characterisation of Electrodes

- Objective:
 - Investigate factors controlling passivation behaviour
 - Define means of diminishing passivation
- Procedure:
 - Use of ca. 30 mm² plate electrodes with various degrees of surface roughness
 - Measurement of electrode potential as function of time in response to applied current density

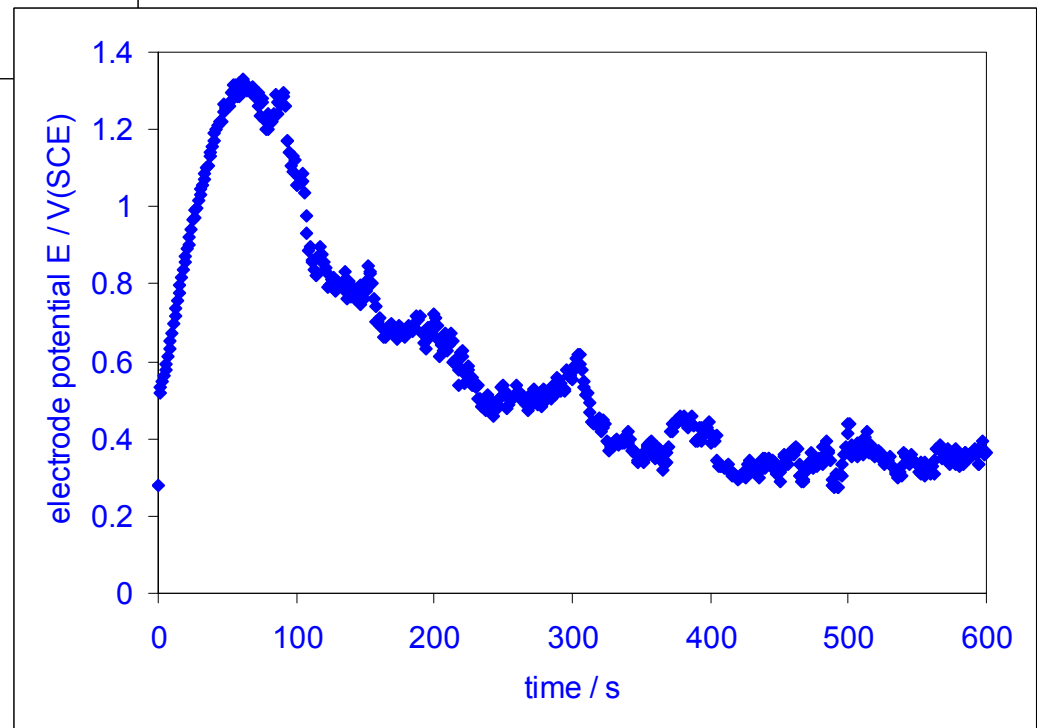
Effect of Surface Roughness



Limit of
potentiostat

Rough Al electrode

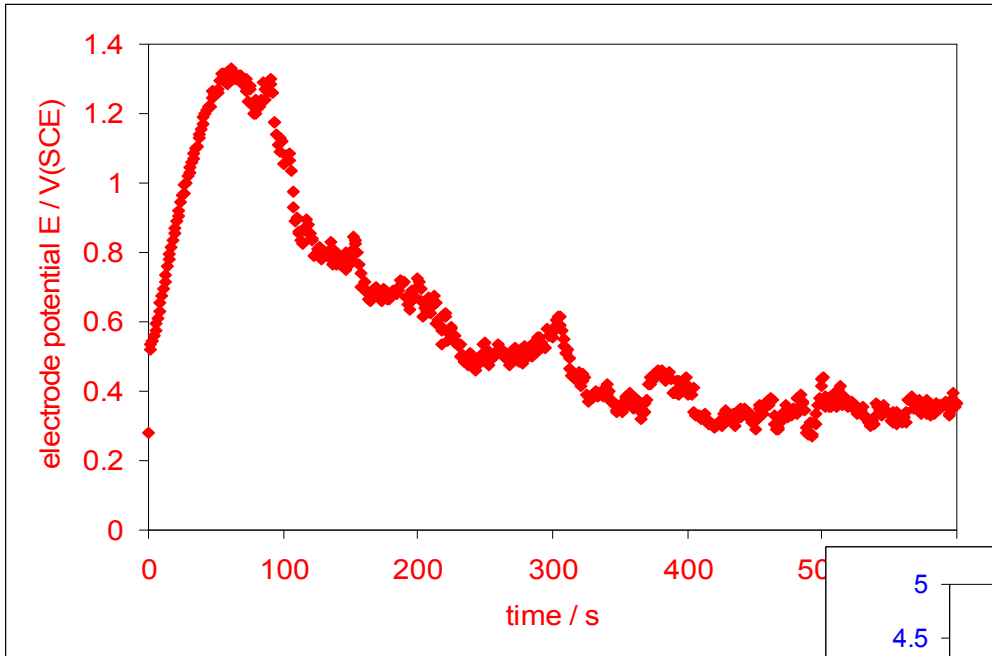
Smooth Al electrode



Solution without Cl⁻

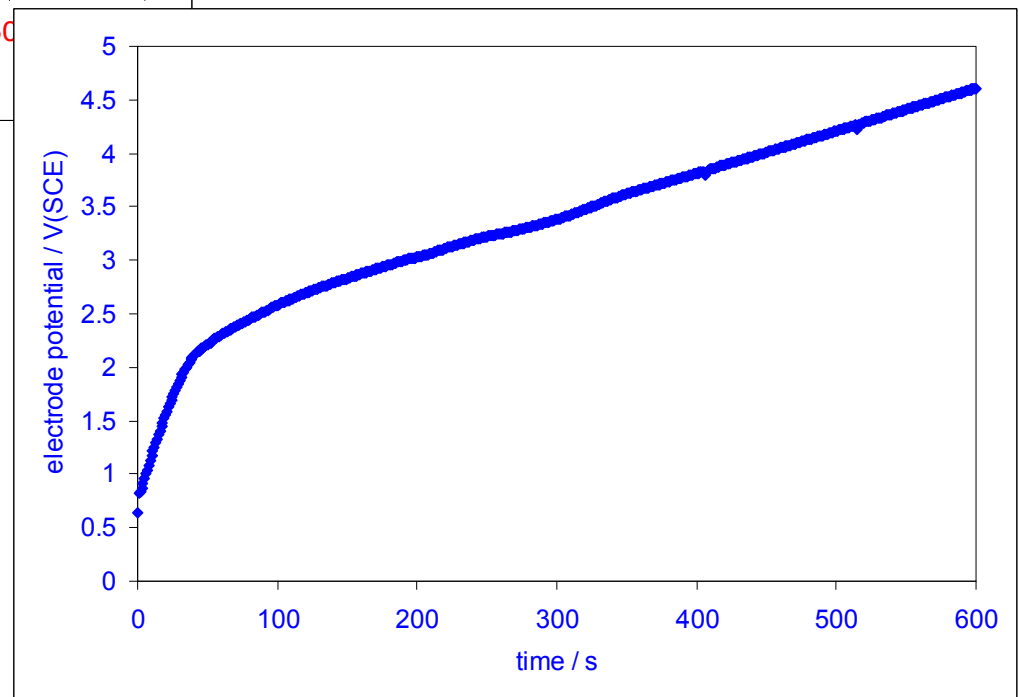
Fresh surface

Effect of Storage Time in Solution



After 72 hours in solution

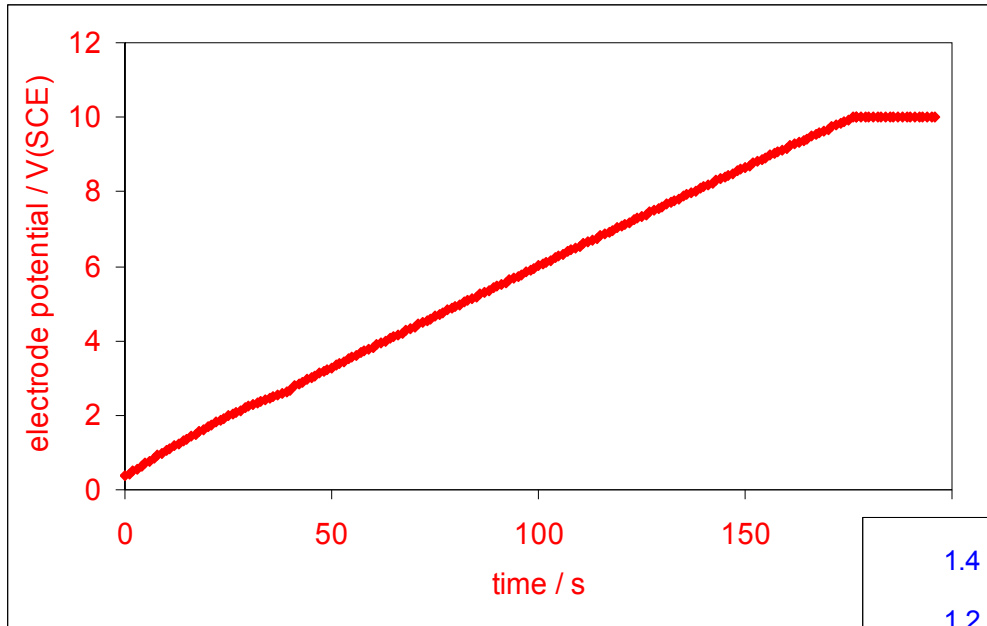
Fresh surface



Rough electrode

Solution without Cl⁻

Effect of Chloride Ions

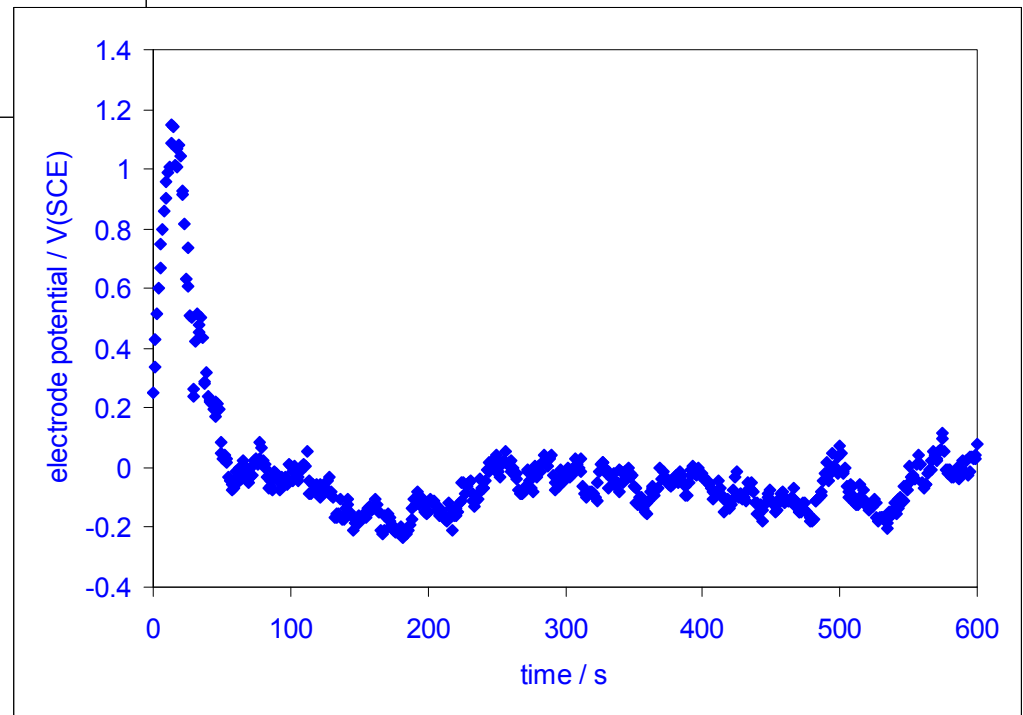


Without Cl⁻

Smooth electrode

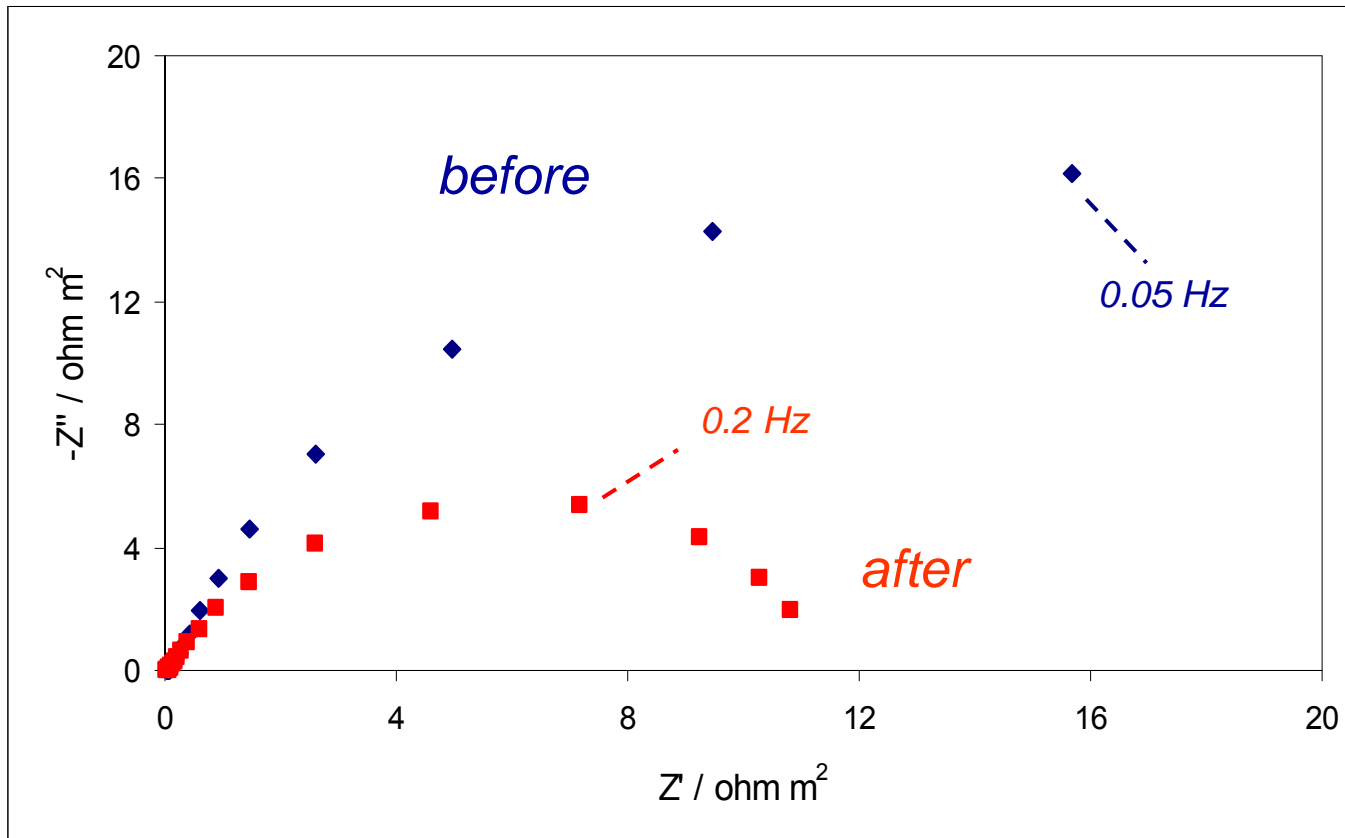
Fresh surface

With Cl⁻



Impedance Spectrum after Corrosion

- Initially, high $-Z''$ (max)-value \rightarrow thick passive layer
- Significantly reduced after constant current \rightarrow layer thinned



$10^4 - 0.05$ Hz

Stationary

High purity Al

Fresh electrode

5×10^{-4} kmol l^{-1}

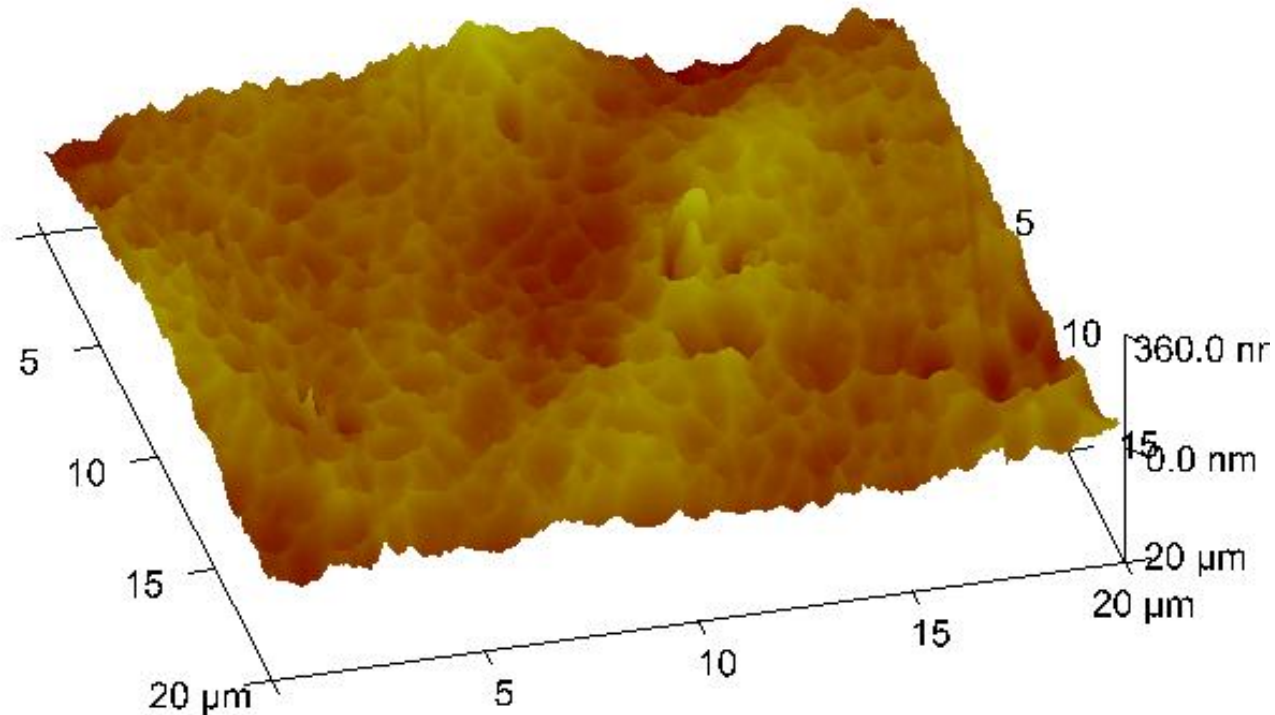
$Na_2SO_4 + 10$ g m^{-3}

humic acid + 1.5×10^{-4}

kmol l^{-1} NaCl

Effect of Real Surface Area of Al Electrode

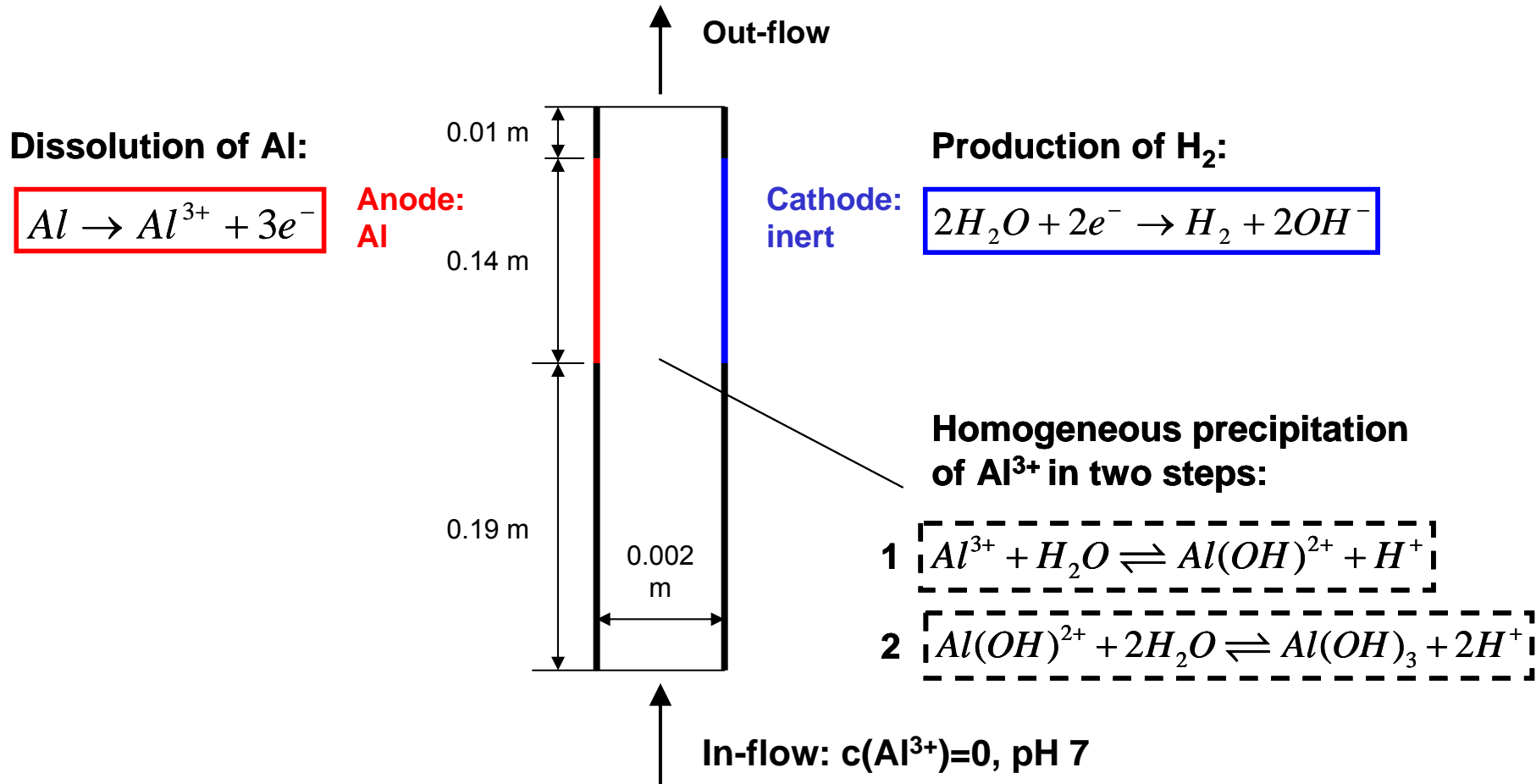
- AFM image of ‘mirror finish’ surface:



- “Micro-roughness” may create cracks in passive layer

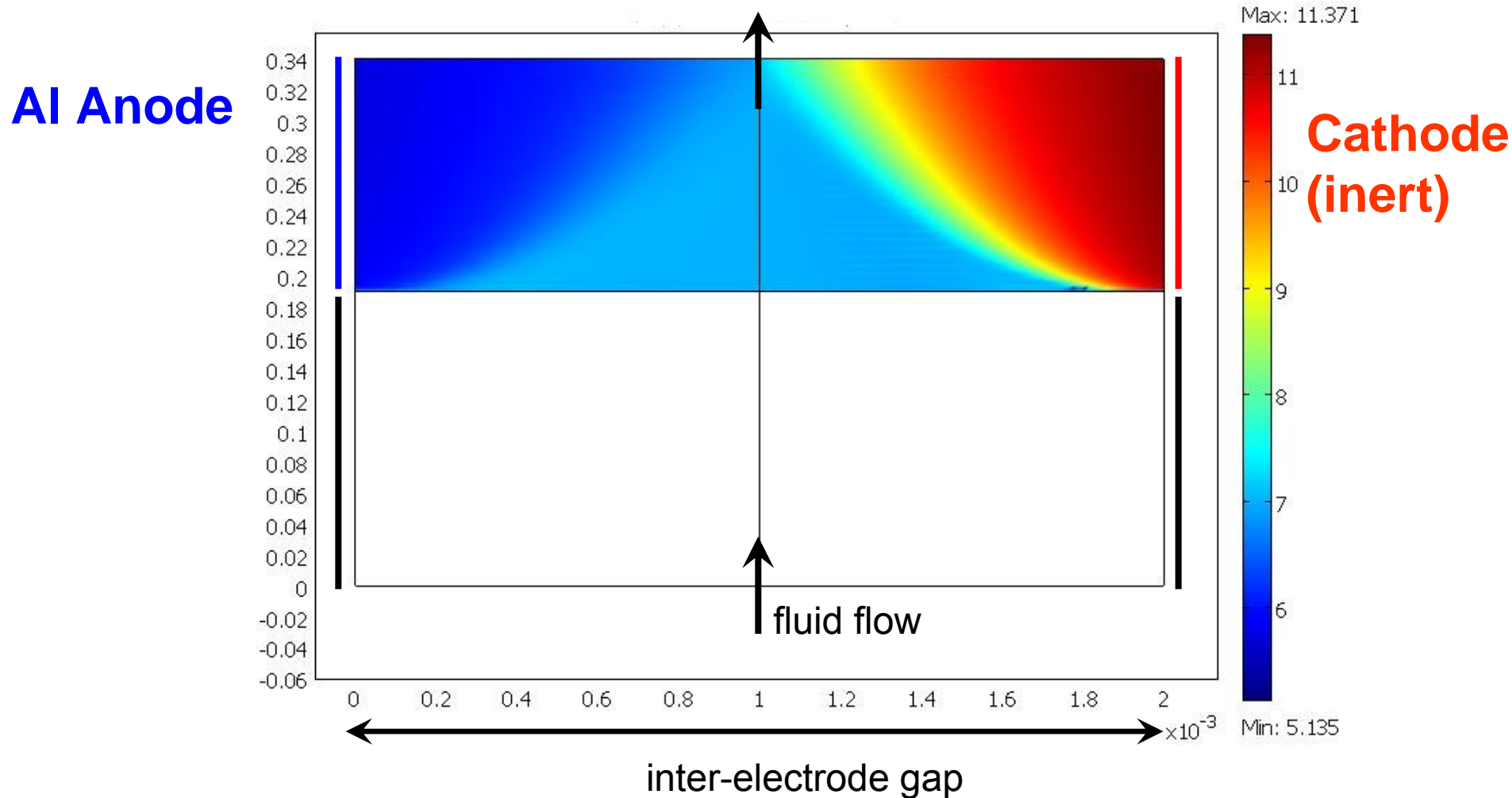
Finite Element Model of Electrochemical Reactor

Reactor design and reactions included:



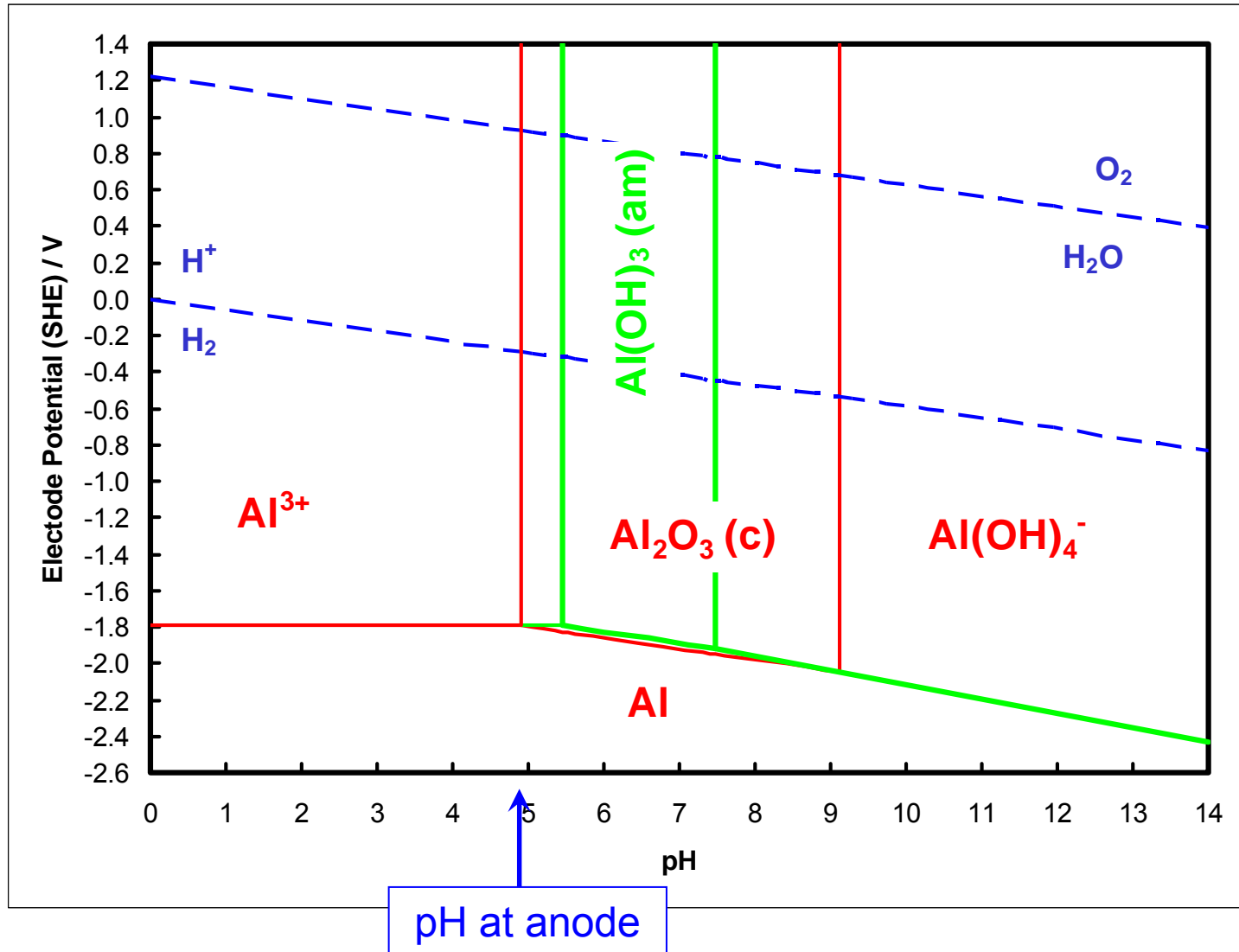
Model Prediction of pH Profile

- Anode Potential +0.05 V(SCE)
- Resultant current density ca. 6.8 A m^{-2}



Effect of pH Profile on Dissolution

- Low local pH at Al anode dissolves oxide layer



Conclusions

- Dissolution of Al anode enabled by low local pH due to Al^{3+} hydrolysis generating H^+ and precipitating $\text{Al}(\text{OH})_3$
- This leads to local dissolution and thinning of passive layer
→ spontaneous depassivation
- Rough and freshly prepared surfaces more likely to exhibit spontaneous depassivation
- Corrosion promoters, e.g. Cl^- , enhance depassivation

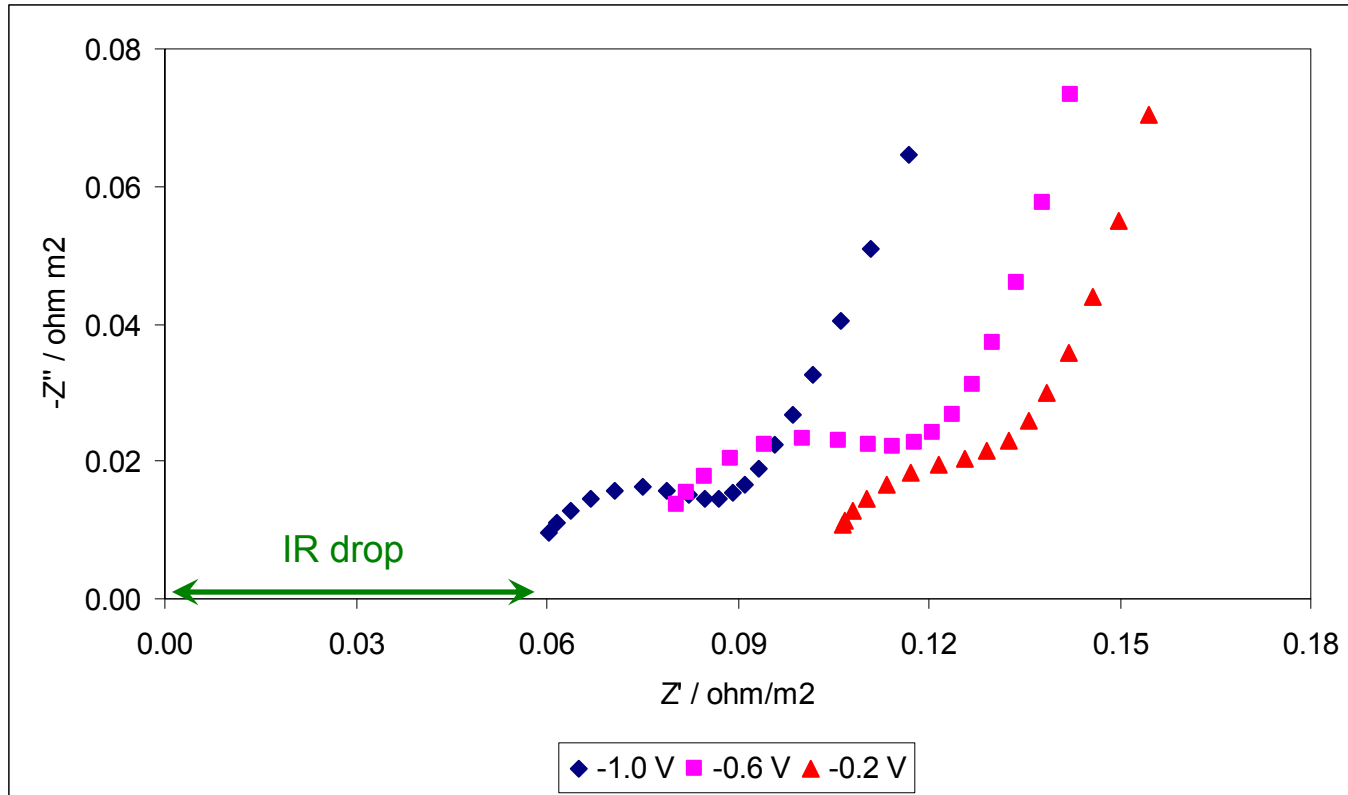
Thanks

- Yorkshire Water, Bradford (UK), for financial support
- Prof. Geoff Kelsall (Imperial College, Dep. of Chemical Engineering)
- Prof. Nigel Graham (Imperial College, Dep. of Civil and Environmental Engineering)

Questions?

High Frequencies

- Frequency range $10^4 - 50$ Hz



Full Spectrum

- Frequency range $10^4 - 10^{-3}$ Hz

