INEOS
Electrochemical Solutions

Advances in Electrode Coatings

AMAI Webinar, August 2021

Todays Agenda

Who we are	Our chlor-alkali capabilities & credentials
Coating Fundamentals	The critical role of electrocatalysts in improving performance
Mini-cell R&D	Agile, rapid, reliable research
CHLORCOAT™	Next generation cathode coatings for chlor-alkali electrolysis
Key Takeaways	3 things to takeaway from todays webinar

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INEOS Electrochemical Solutions

Designed **for life.**

Who We Are

INEOS Group Overview

$61 bn Sales

26,000 employees

36 Businesses

66 million tons of chemicals capacity

20 million tons of refinery products (420,000 bbls/day)

26 million boe per annum

194 manufacturing sites worldwide

29 Countries

84 sites in Europe

25 sites in Asia

80 sites in Americas

5 sites in ROW

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Who We Are

A major global supplier of industrial electrochemical technologies

INEOS Electrochemical Solutions

We Research & Develop World Class Electrochemical Products

- FM & BICHLOR™ electrolysers
- CHLORCOAT™ coatings

We Sell Electrolysers, Associated Parts & Technical Services

- 4 generations of electrolyser technology, installed globally

We Refurbish & Re-coat Electrolyser Structures

- IES Technology (Aftersales)
- Third party technologies

www.ineos.com/electrochemical

40 Years of Innovation

- Long history of bringing product improvements to the industry:
  - Multiple generations of electrolysers developed
  - Numerous technology patents generated
  - Installations in over 30 countries

- We operate our own electrolyser plants, so we understand chlor-alkali:
  - Coatings are a critical factor in successful plant performance
  - Future improvements / big efficiency gains will come from coatings

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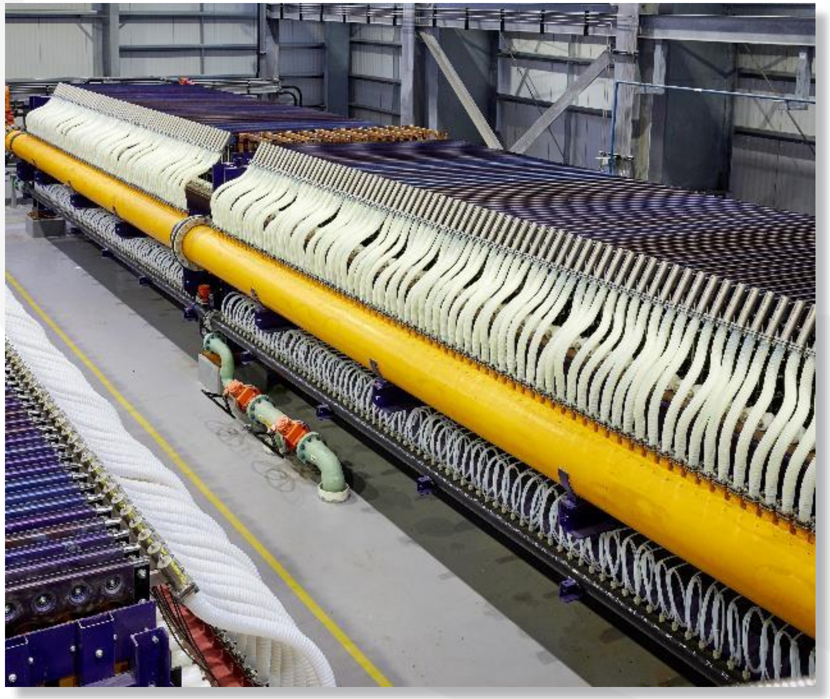
INEOS BICHLOR™ Electrolyser

Significant energy savings and long-lasting performance over a lifetime of chlor-alkali production.

- Less than **1990* kWh/te NaOH** @ 6kA/m^2 power consumption
- Class leading output of **69,000 MTPA NaOH** per electrolyser**
- Largest effective working area of **3.4m^2** per module means fewer modules are required per tonne of NaOH
- Zero gap, “modular” bipolar design delivers full use of the membrane area and extends the membrane’s life
- Robust, safe construction with superior strength and resistance to damage and distortion
- Widest operational pressure range, (atmospheric to 400mbarg) - all operator requirements can be met



* Expected value @ 385mbarg Cl_2, 90°C and 32wt% NaOH **Based on 350 days operation and 7kA/m^2

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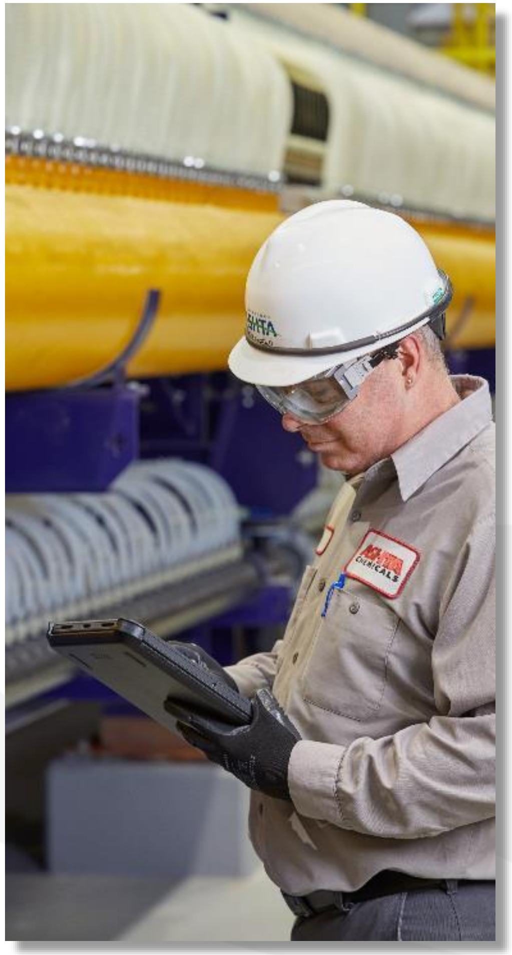
BICHLOR™ Electrolyser Installations



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Coating Fundamentals

Introduction – Trevor Davies

- Senior Electrochemist at INEOS Electrochemical Solutions, Trevor has a wealth of experience across electrolysers, fuel cells, redox flow batteries, sensors, simulations and electrochemical instrumentation.
- Graduated from Oxford University in 2002 with first class honours in Chemistry, followed by a doctorate in Electrochemistry in 2005 (also at Oxford).
- Through his career he has generated 12 patents and published over 40 articles in international journals on topics ranging from electrochemical energy conversion/storage to sensors for DNA methylation.
- Trevor has also held positions in research at Shell and as a University Lecturer.

What Drives Chlor-Alkali Coating Development?

Properties of a good (electro)catalyst

Activity	→	"Fast" kinetics, high surface area	→	Cell voltage
Selectivity	→	Minimize unwanted side reactions	→	Anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$
Durability	→	Adhesion, passivation, "corrosion"	→	Reverse current, alkaline wear
Cost	→	Raw materials and fabrication	→	Iridium, ruthenium, platinum
Handling	→	Toxicity, ease of preparation, waste	→	Precursors and coating methods
Conductivity	→	Provide path for electrons	→	Cell voltage

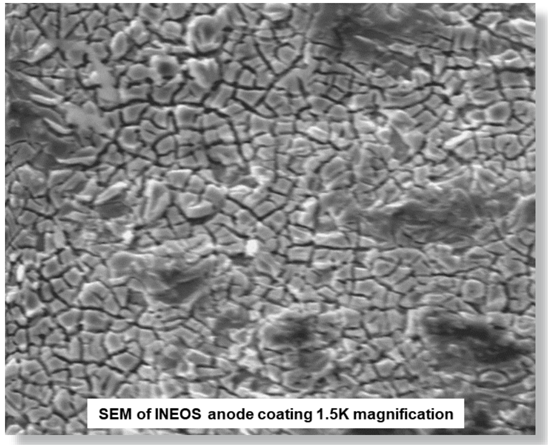
Process Fundamentals

$2\ NaCl + 2\ H_2O \rightarrow 2\ NaOH + Cl_2 + H_2$

Anode

$2\ NaCl \rightarrow 2\ Na^+ + Cl_2 + 2\ e^-$

- Ti substrate with catalyst coating
  - Key components RuO_2 and IrO_2
  - Cracked surface
- O_2 production competes



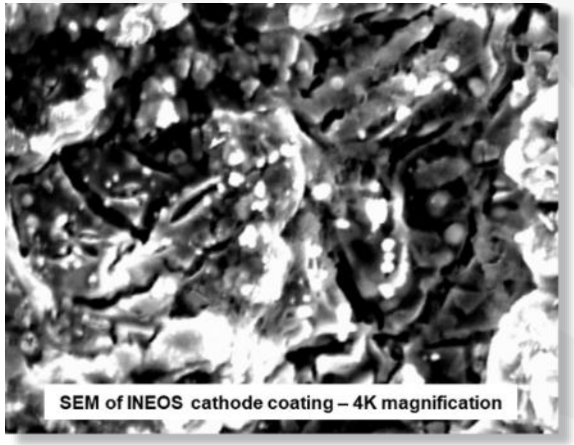
SEM of INEOS anode coating 1.5K magnification

Cation exchange membrane promotes transfer of Na^+ to catholyte

Cathode

$2\ H_2O + 2\ e^- \rightarrow 2\ OH^- + H_2$

- Ni substrate with catalyst coating
  - RuO_2 , Pt-group, NiOx
  - Thickness can vary (1-200 mm)



SEM of INEOS cathode coating – 4K magnification

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Mini-cell R&D

INEOS Mini-cell Testing Facilities

Investment in new innovative test stations supports faster coatings research and development

Enhanced experimentation

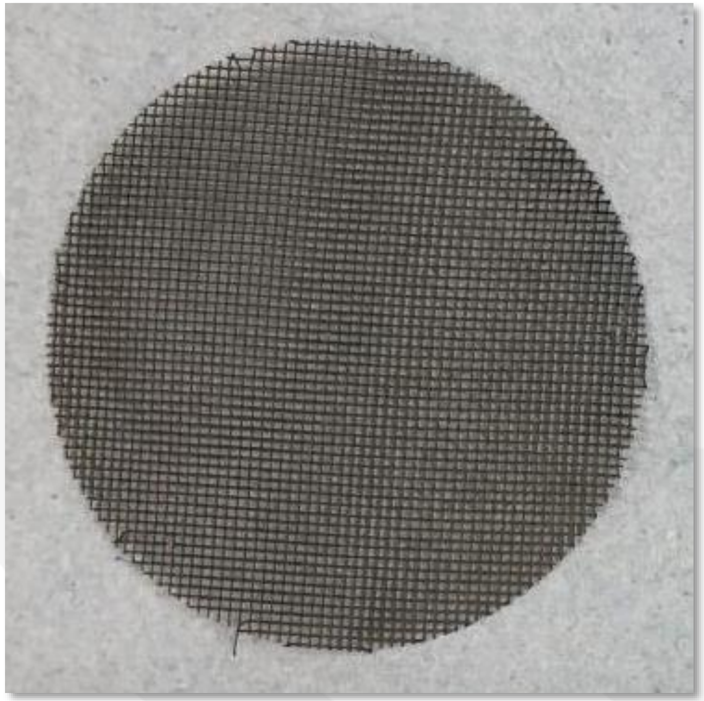
- Small mesh electrodes are quickly fabricated in-lab
- High throughput design allows 200+ electrode tests per year

Exceptional control

- Cell temperature and feed electrolytes are precisely controlled
- No requirement to “normalise” experimental data

Fundamental insights

- Use of potentiostat allows rapid sampling of current-voltage data and electrochemical impedance spectroscopy
- Reference electrode provides valuable data on electrode performance



INEOS Mini-cell Testing Applications

Polarisation and electrochemical impedance spectroscopy

- Standard method to determine electrode performance
- Impedance allows insights into voltage gains of electrolyser
- Reference electrode produces data on cathode performance

Constant current overnight operation (6kA/m^2)

- Electrode performance, electrolyte sampling and O_2 in Cl_2
- Current efficiency

Reverse current tests

- Multiple cell “shorts” provide a good insight into coating durability
- Measure the coating loss via XRF
- Measure coating loss in exit electrolyte

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INEOS Mini-cell Testing Facilities

Zero-gap cell composed of plates compressed together with a piston

- Based on plate type design enabling quick build (30mins) for agile experimentation
- Zero-gap chlor-alkali cell to replicate real-world performance
- Reference electrode access to cathode to attribute and analyse voltage contributions
- Process conditions precisely controlled to minimise errors from corrections and normalisation

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Mini-cell Orientation

- Electrolyte flow controlled using peristaltic pumps
- Electrolyte pre-heated before entering cell
- Cell load controlled with a 10A potentiostat
- Cell temperature controlled
- Chlorine produced is scrubbed

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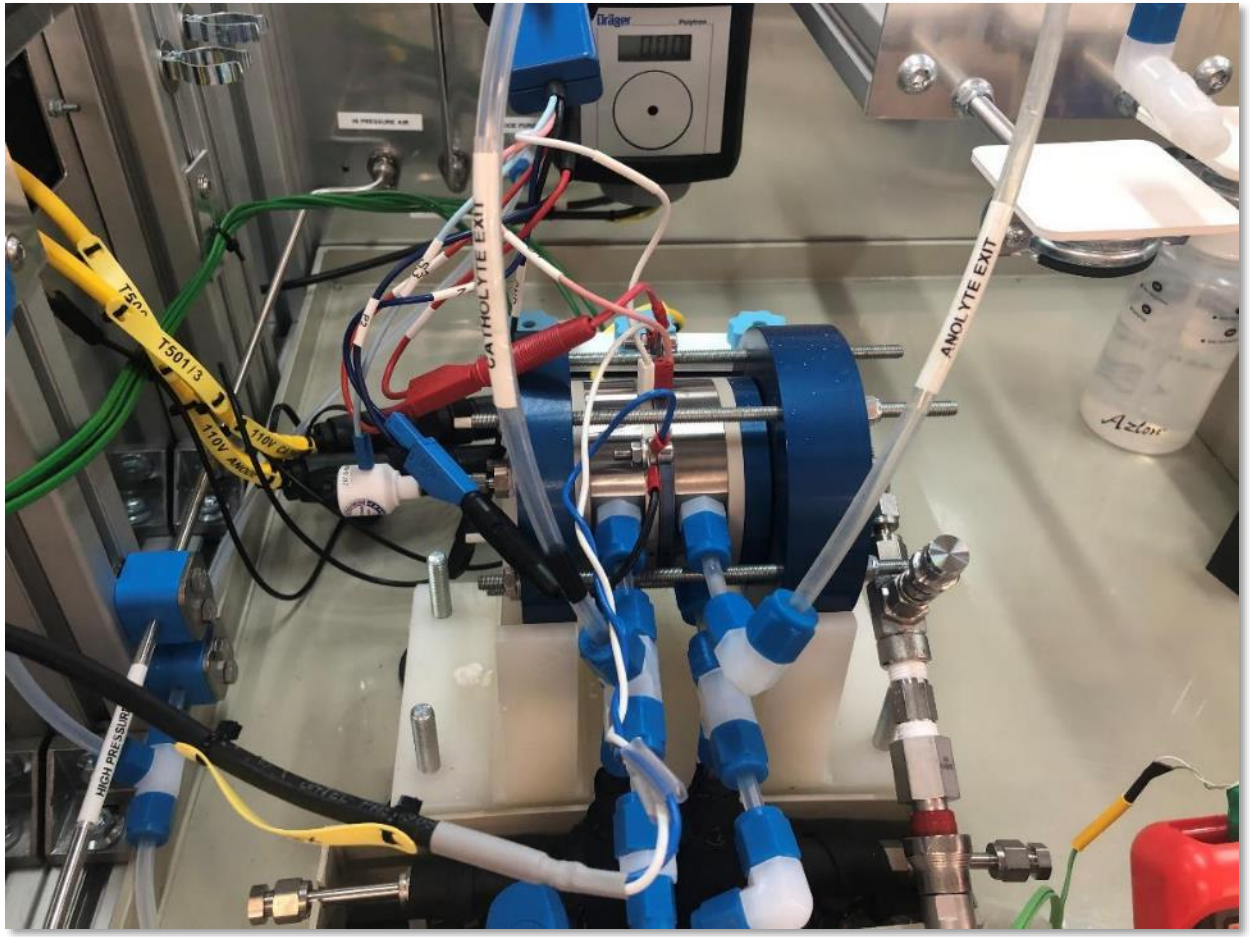
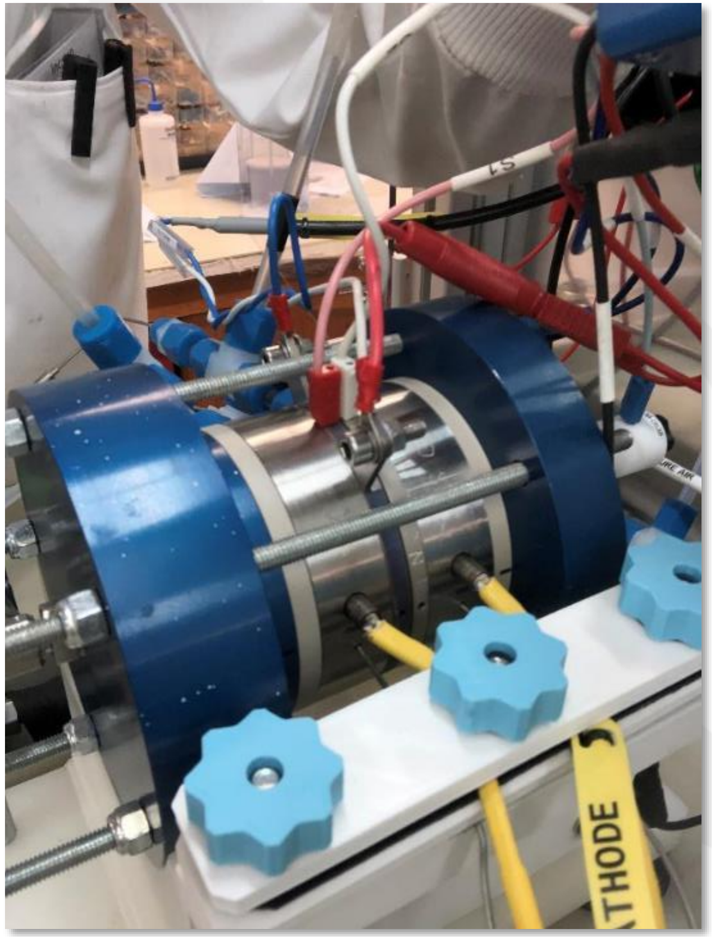
Mini-cell Orientation

Front view of cell



Rear view of cell



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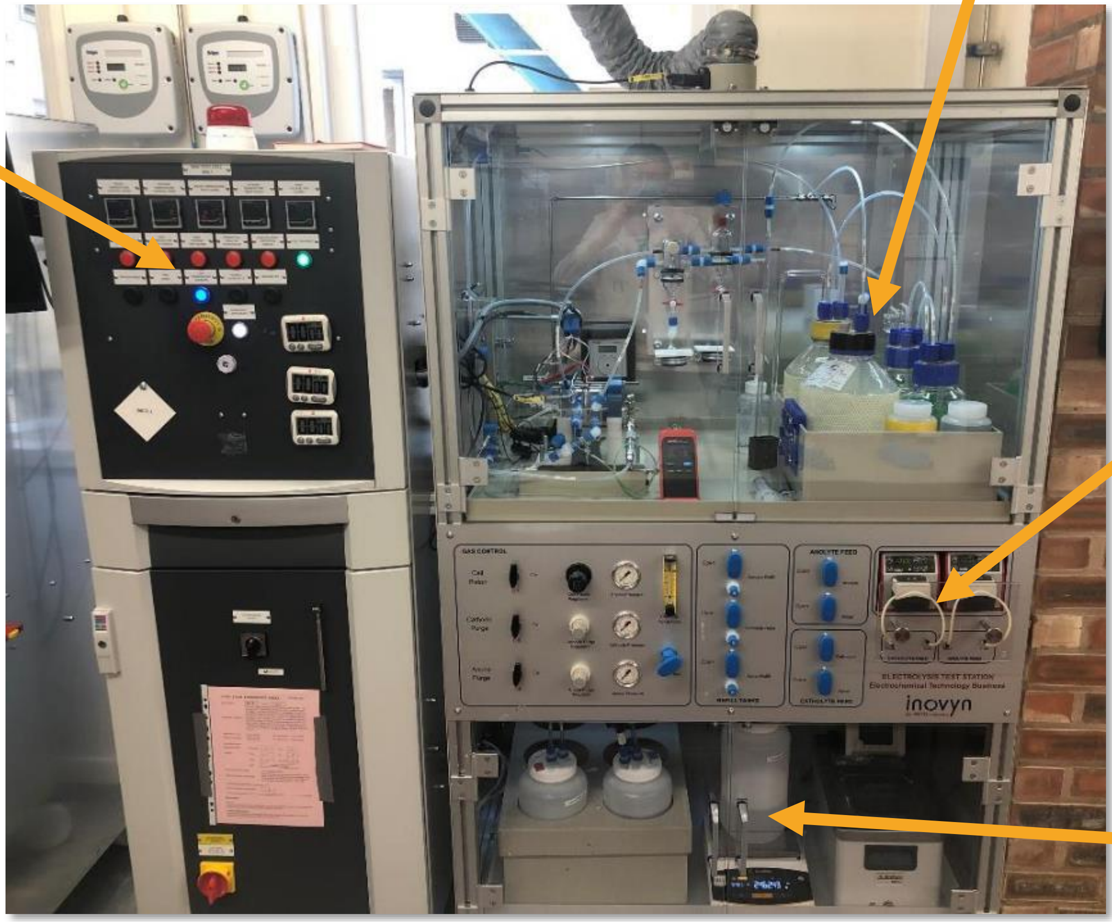
Mini-cell Orientation

Control panel

Effluent management



Precision flow control

Mass balance

Electrolyte and gas sampling

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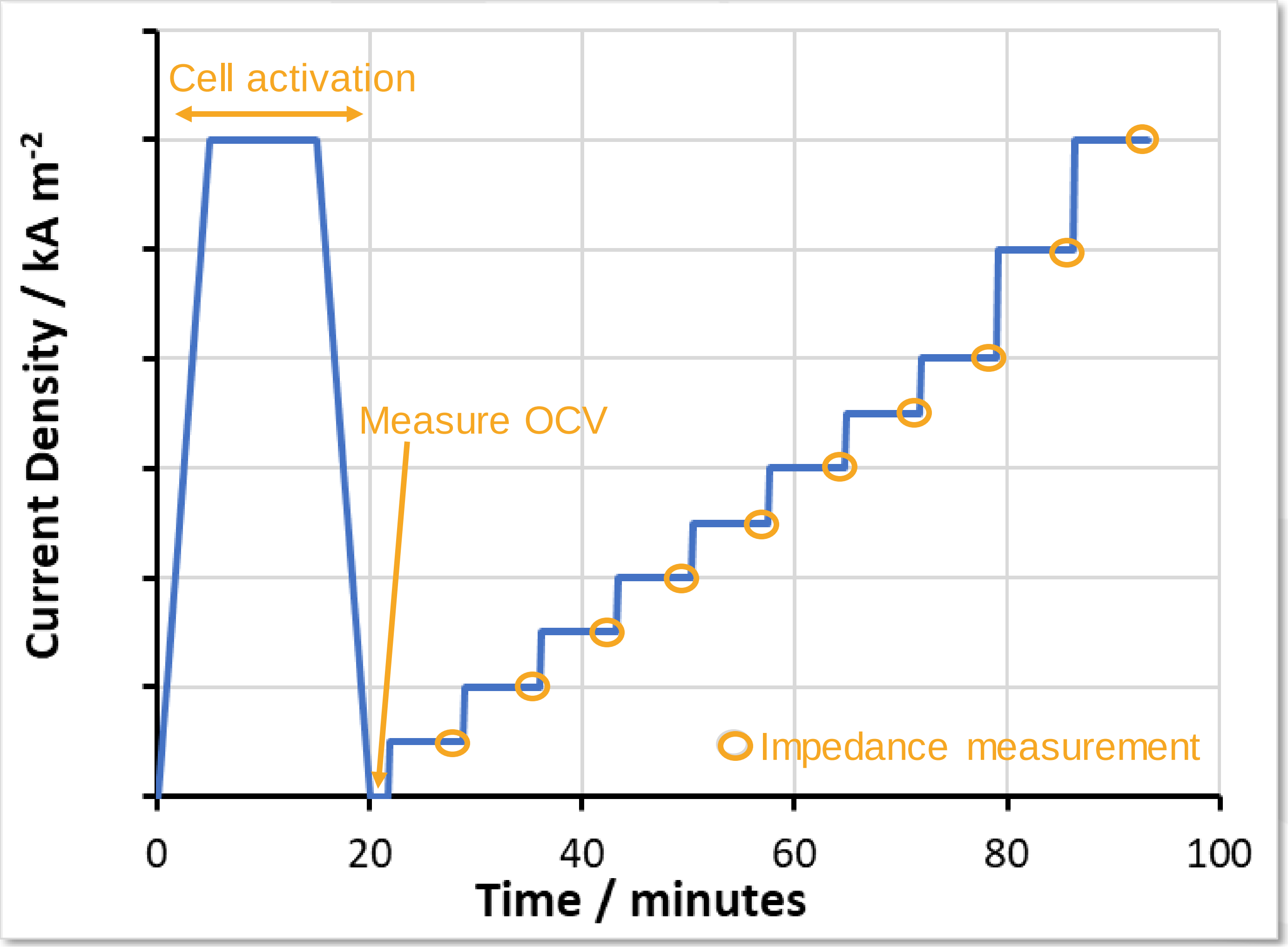
Polarization & Electrochemical Impedance Spectroscopy

Main test for cell performance

- Initial ramp to 6kA/m^2 to activate electrodes followed by open circuit
- Current steps to measure cell and cathode voltage followed by electrochemical impedance spectroscopy
  - F8081 membrane (AGC)
  - CHLORCOAT anode
  - 29.3% caustic feed (~32% exit)
  - 300gpl alkaline brine feed (~200gpl exit)
  - 85°C cell temperature



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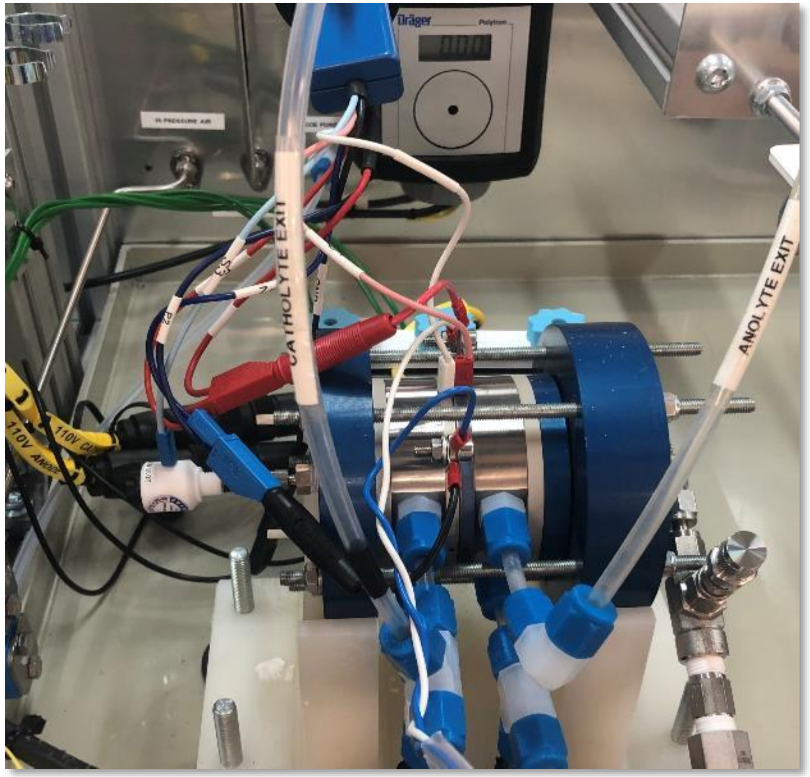
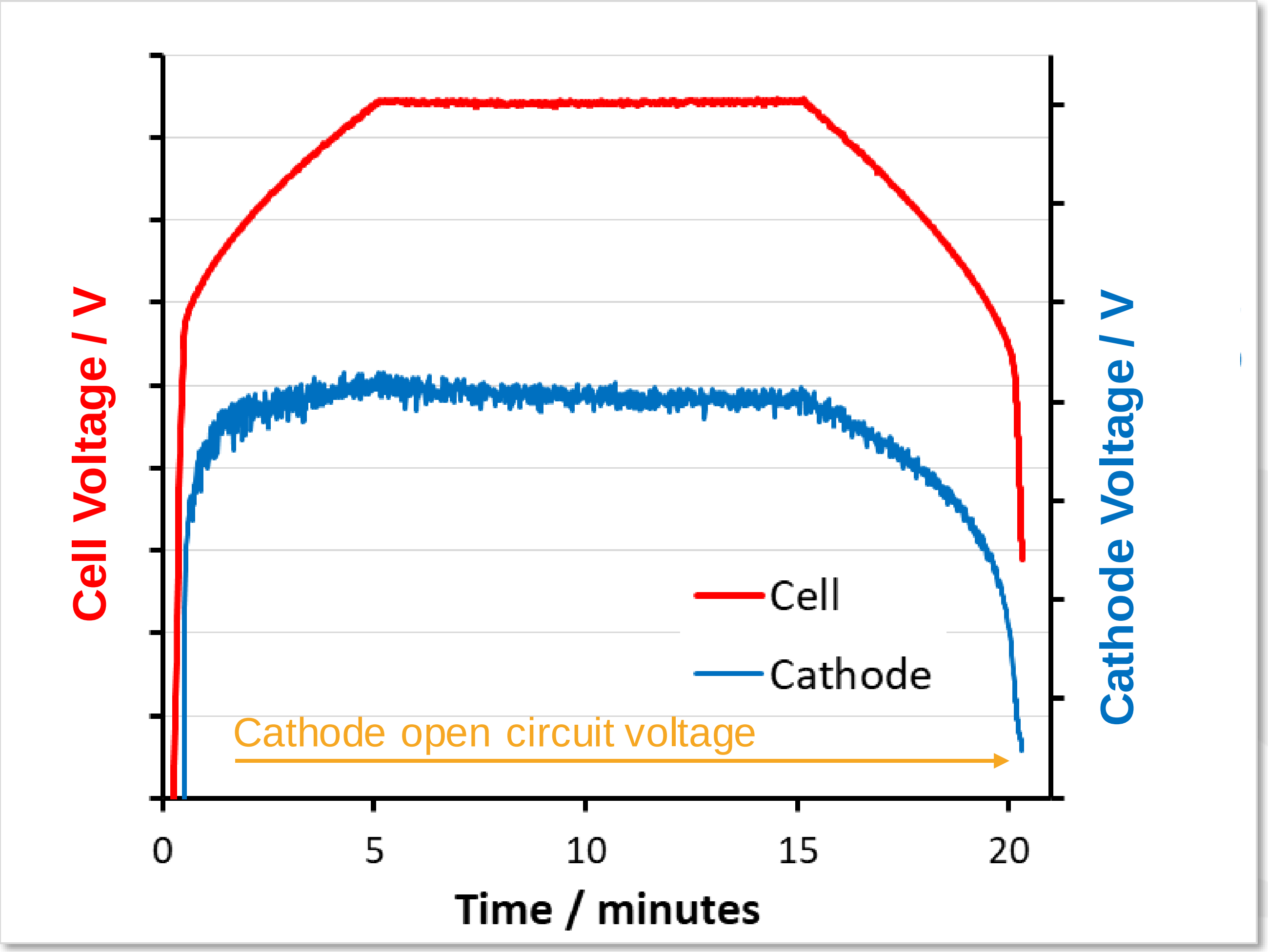
Initial Polarization

Cell Voltage = red - white

Cathode Voltage = blue - white



cathode overvoltage = cathode voltage – cathode open circuit voltage



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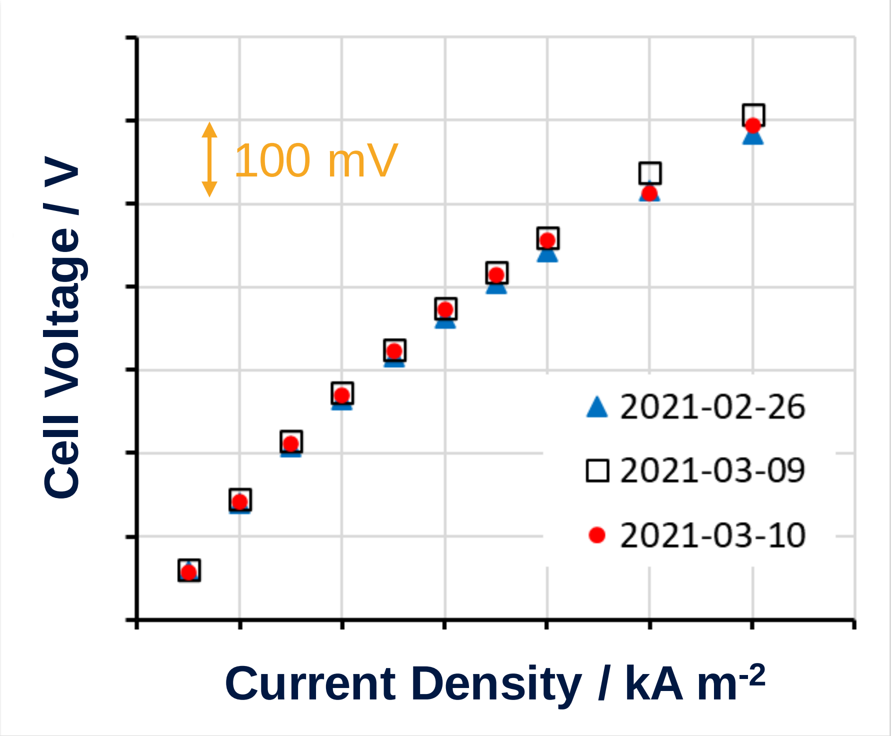
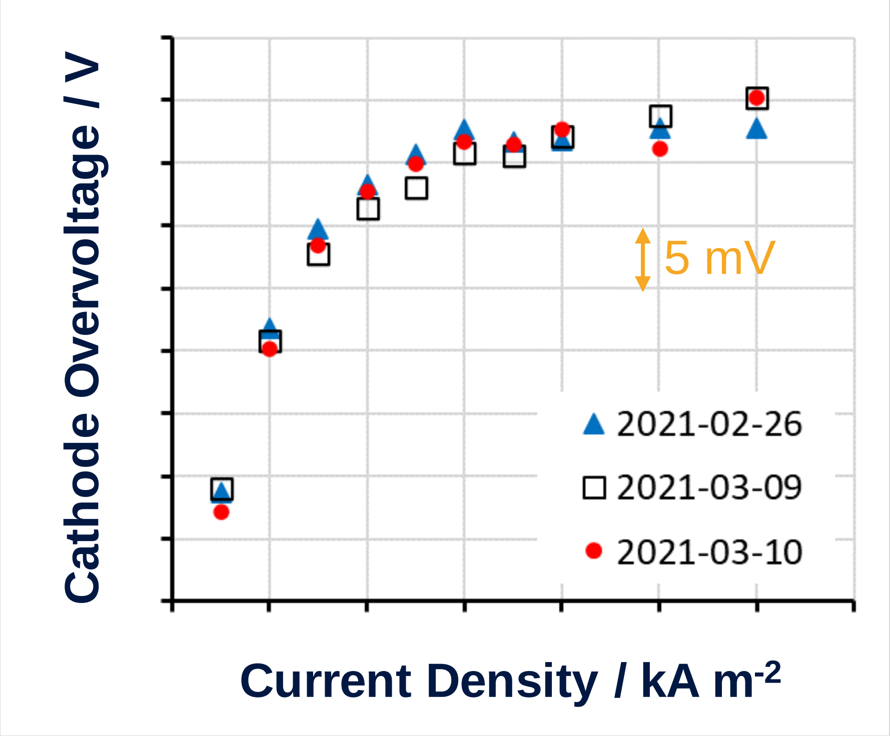
Initial Polarization

Optimised cell build and control of electrolyser conditions = good repeatability

- Three different cell builds (same electrodes, membrane) produce relatively low scatter
- Larger differences can be allocated to cell ohmic resistance via impedance measurements





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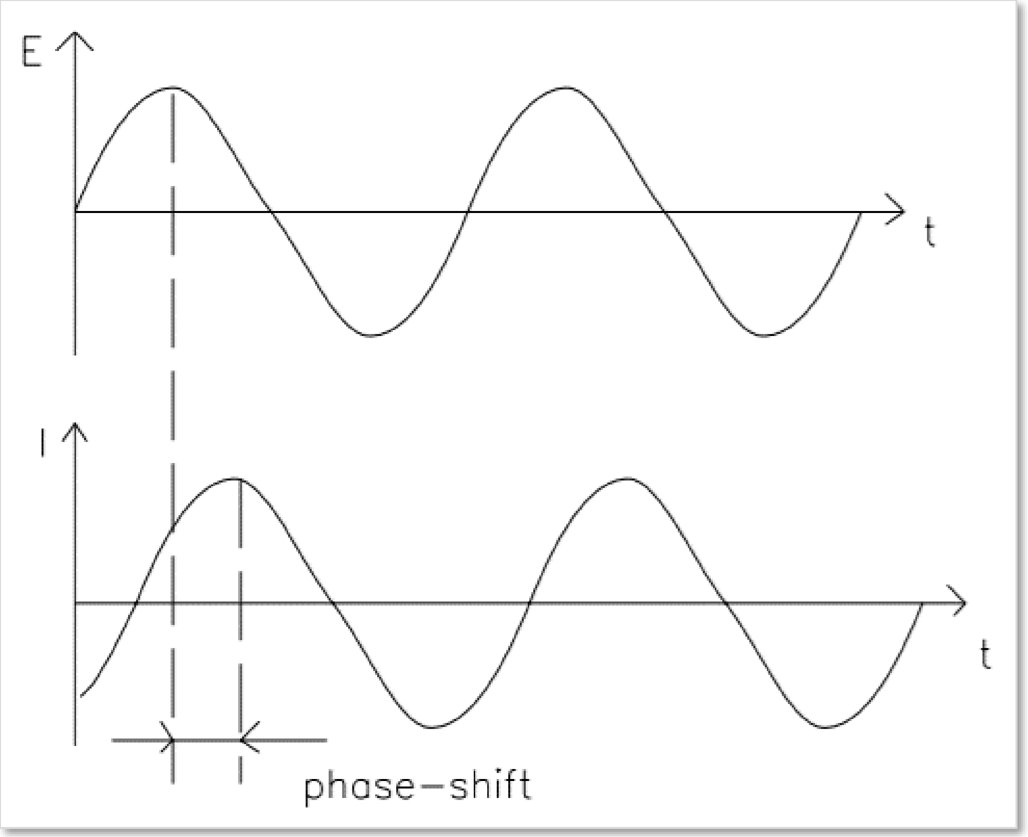
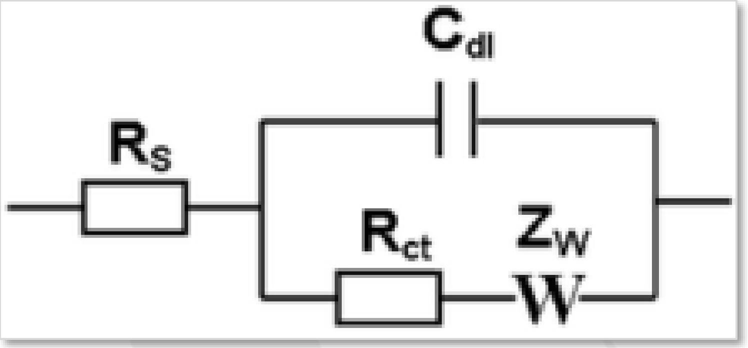
Electrochemical Impedance Spectroscopy – An AC Technique

Direct Current → Resistance

Alternating Current → Impedance

$$R = \frac{V}{I}$$



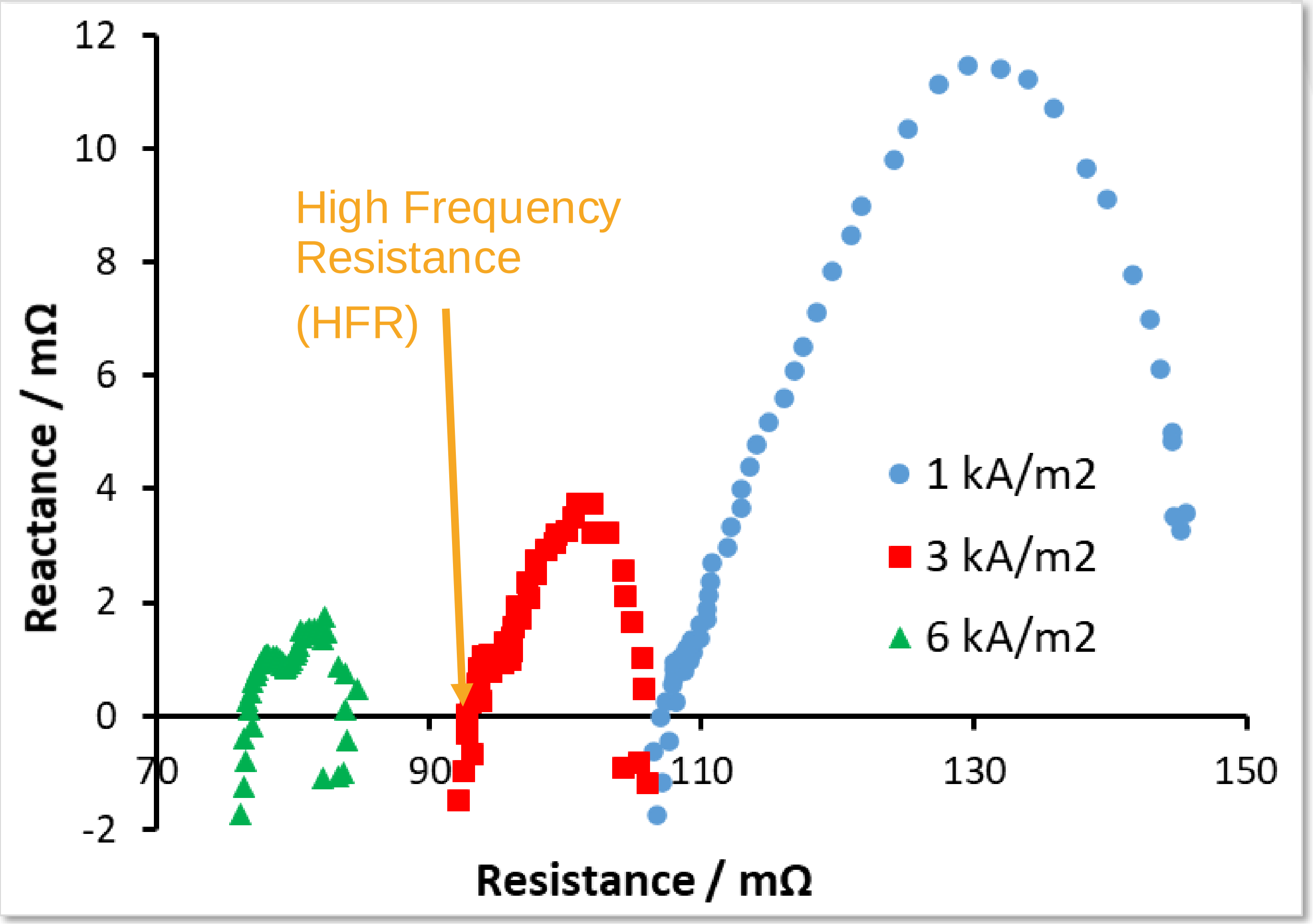


Every electrochemical cell can be described as a combination of circuit elements

- The impedance of some of the elements is dependent on the frequency of alternating current
- Measure the impedance and phase shift of the cell at different frequencies (100MHz – 0.1Hz)
- Allows us to determine cause of voltage gains in an electrolyser

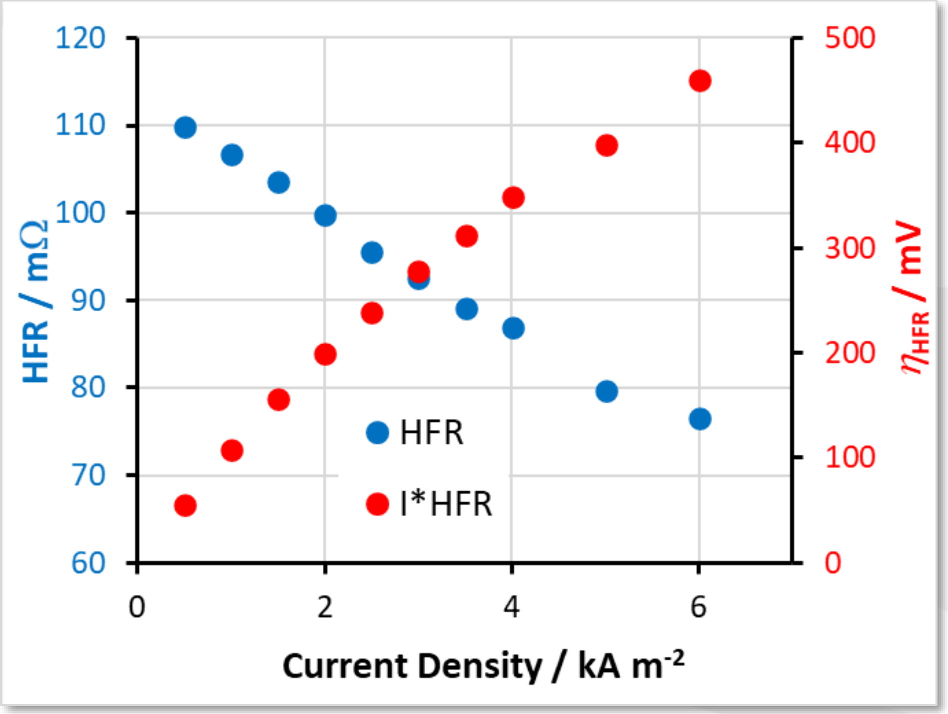
Electrochemical Impedance Spectroscopy - Cell

The high frequency resistance is the cell ohmic resistance, dominated by membrane

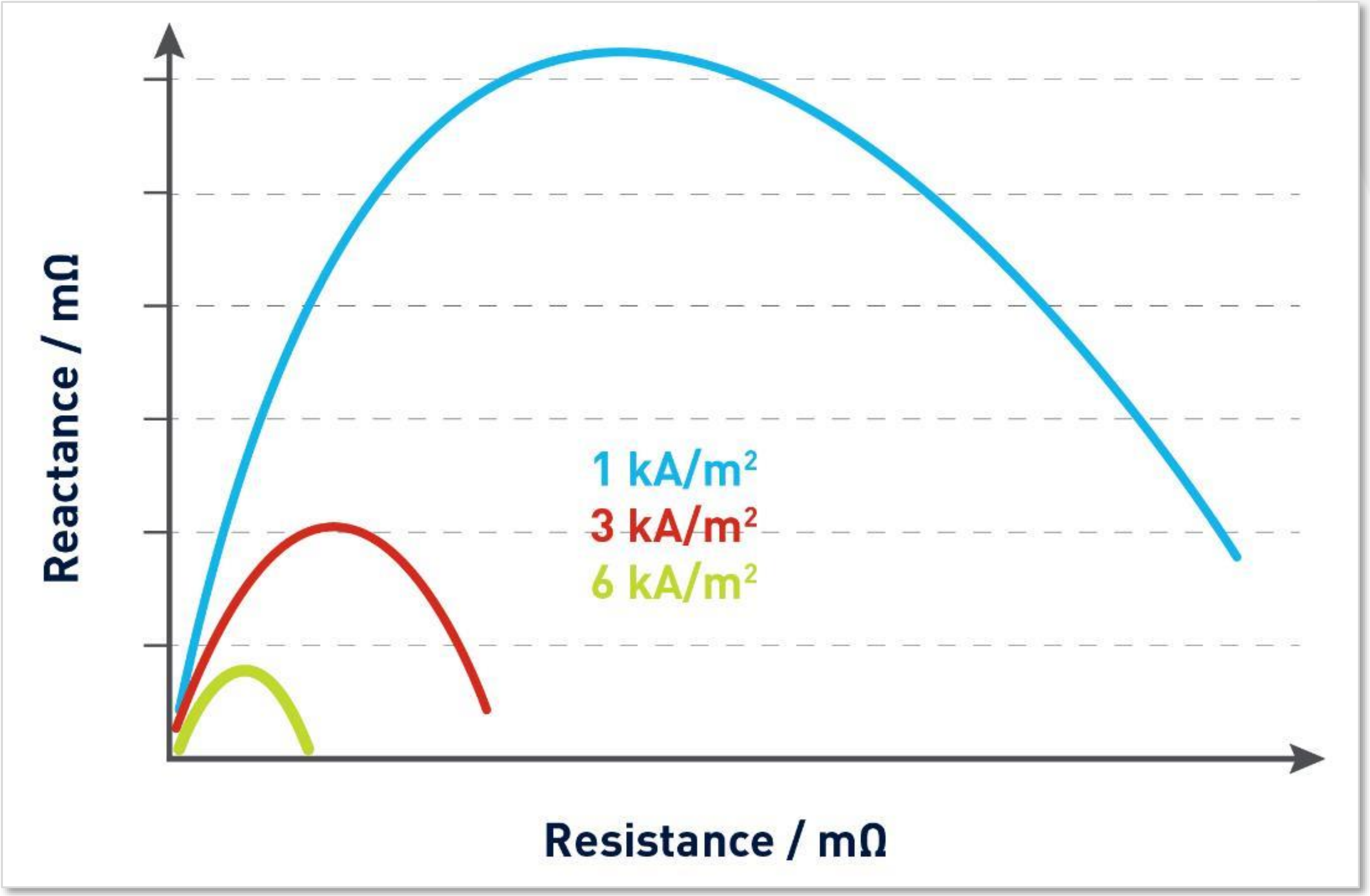


η_{cell} = operating voltage – open circuit voltage

$\eta_{cell} = \eta_{HFR} + \eta_{cathode} + \eta_{anode}$



Electrochemical Impedance Spectroscopy - Cathode



Can also perform impedance between the reference and cathode

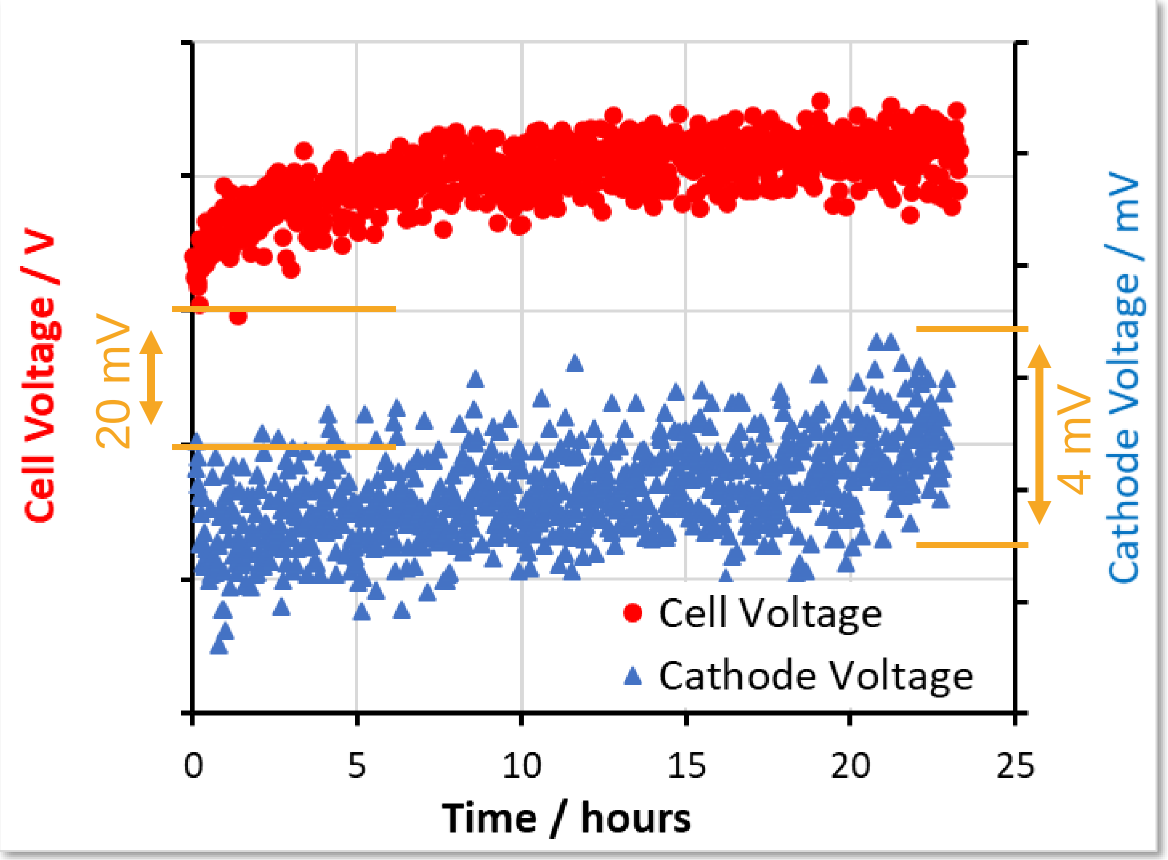
- Gives valuable information on the cathode kinetics and surface area
- HFR is tiny because the reference is very close to the cathode

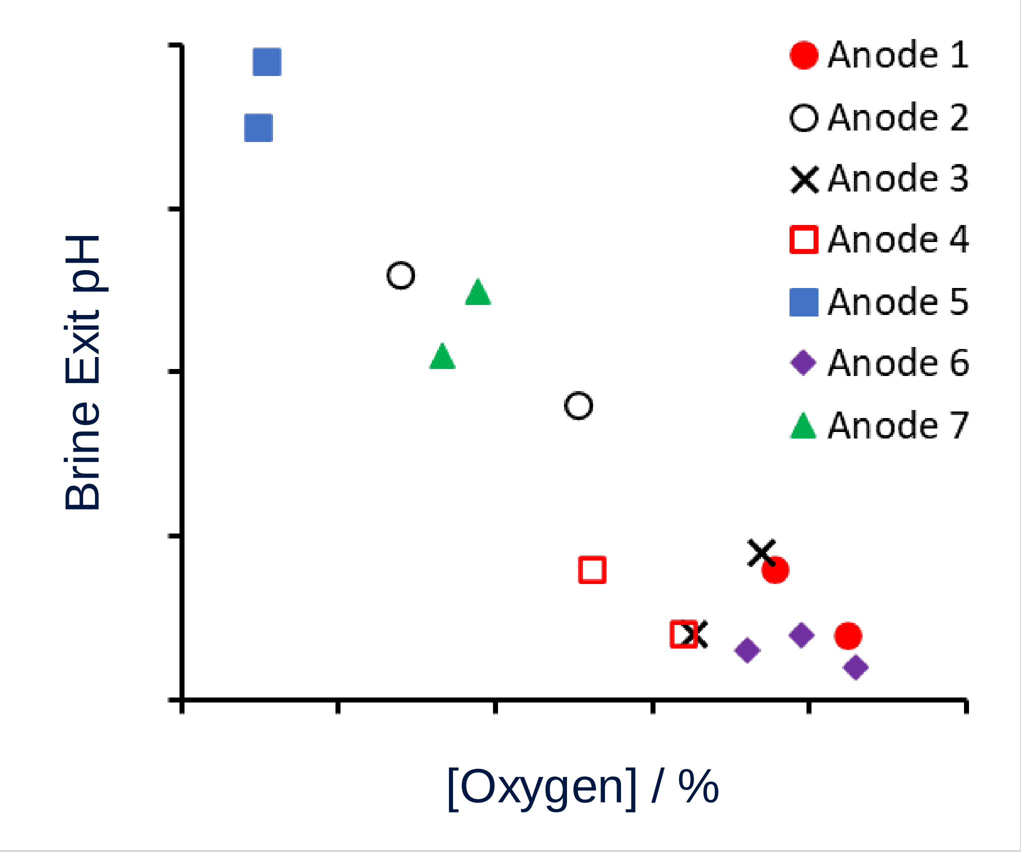
Constant Current Operation

Hold at $6 kA/m^2$ for 23 hours

- Sample chlorine gas and exit electrolytes

$$4\,OH^- \rightarrow O_2 + 2\,H_2O + 4e^-$$





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Current Efficiency (Hydroxide)

$$CE_{\mathrm{NaOH}} = \frac{\text{NaOH production rate}}{I/F}$$

The use of a small cell allows easy determination of current efficiency

- "Sulphate Key" is the method recommended by INEOS Electrochemical Solutions
  - Involves chemical analysis of feed and exit brine
- Mass balance allows accurate determination of NaOH feed flow rate
  - Measure NaOH feed and exit densities to directly determine NaOH production rate

Compound	Feed Brine	Depleted Brine
NaCl	303 g L^{-1}	210 g L^{-1}
$NaClO_3$	0.15 g L^{-1}	0.07 g L^{-1}
NaOCl	-	1.44 g L^{-1}
Na_2SO_4	3.84 g L^{-1}	5.06 g L^{-1}
NaOH	0.005 g L^{-1}	-

Gas analysis: O_2/Cl_2 = 0.012

CE_{NaOH} = 97.4%

NaOH inlet flow	Inlet ρ_{NaOH}	Exit ρ_{NaOH}	Current
31.36 mg s^{-1}	1.3204 g cm^{-3}	1.3449 g cm^{-3}	5.992 A

CE_{NaOH} = 97.2%

Reverse Current

Reverse currents occur during (uncontrolled) shutdowns

- Cells act as “charged batteries” discharging with oxidation at the cathode and reduction at the anode
- Leads to dissolution of metals and loss of coating

Our mini-cell can mimic this situation by suddenly shorting whilst under load

- Relative test, very harsh and causes some form of damage to any cell
- Controlled shorting of cell with rapid sampling of current voltage data
  - The potentiostat accurately measures the charge transferred in each reverse current event
- Perform a number of cycles
  - Monitor change in cell operating voltage
  - Measure coating loss via XRF and ICP of exit caustic

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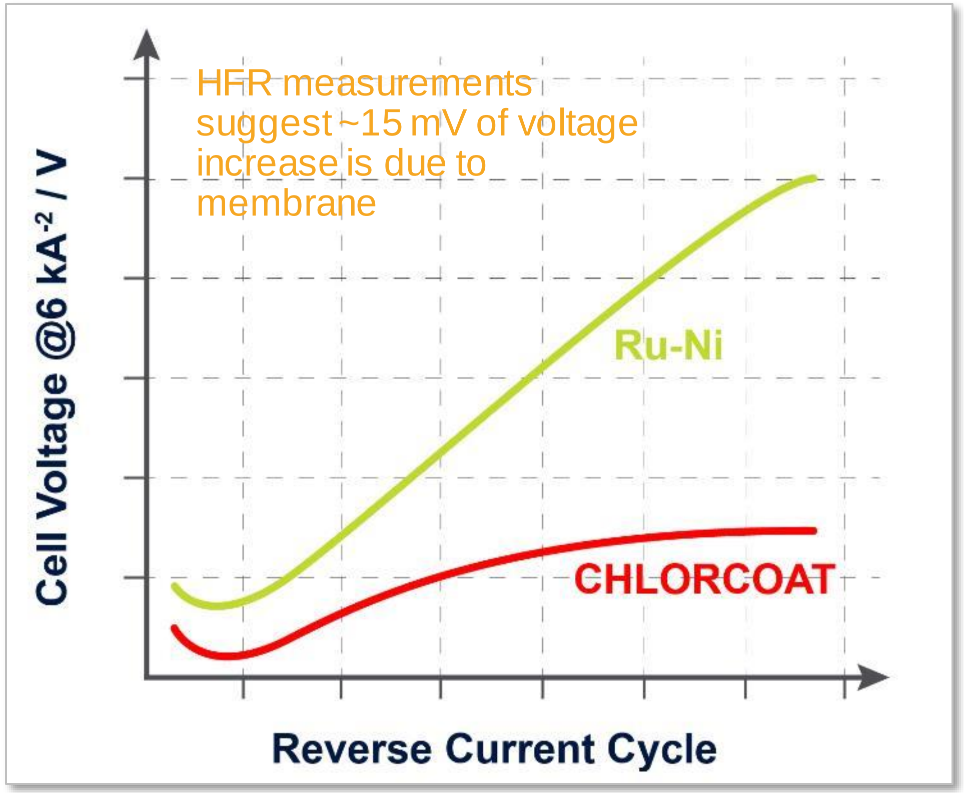
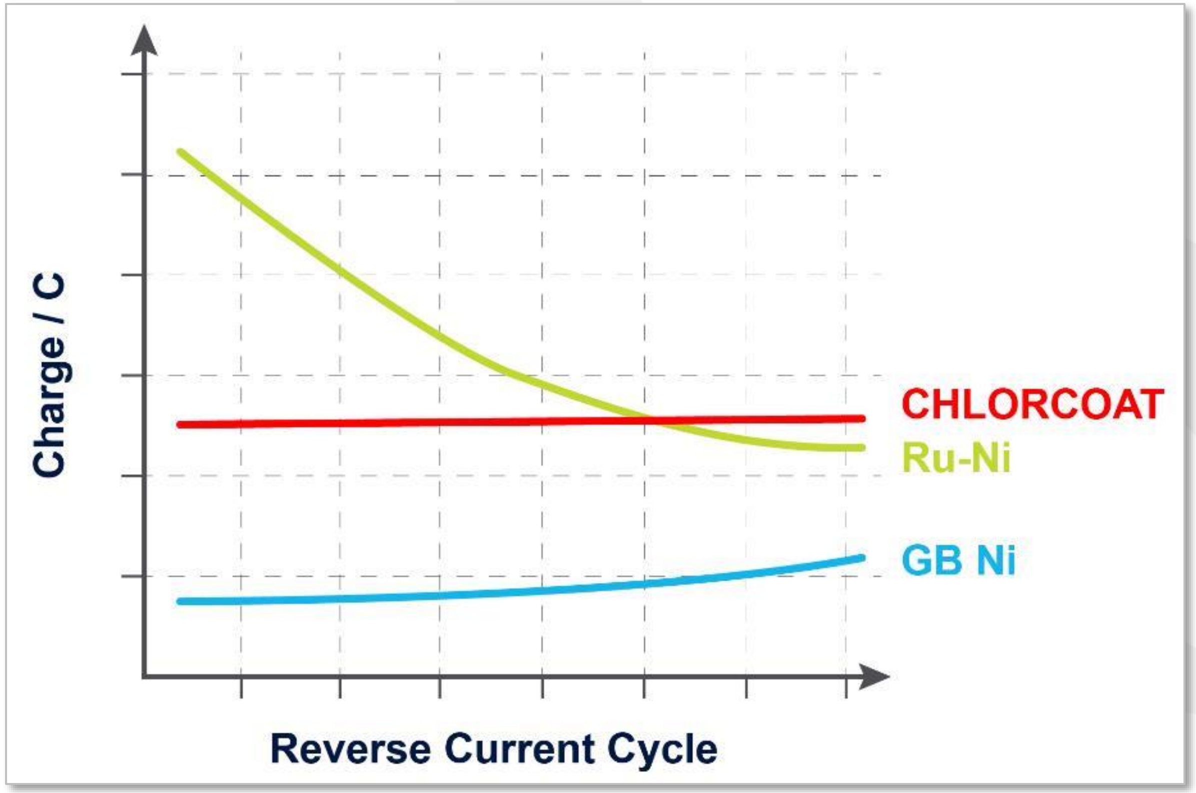
Reverse Current Testing

	Cathode coating loss (XRF)	Exit NaOH analysis (ICP)
CHLORCOAT	1%	<2 ppm precious metal
Ru on Ni	85%	40 ppm Ru





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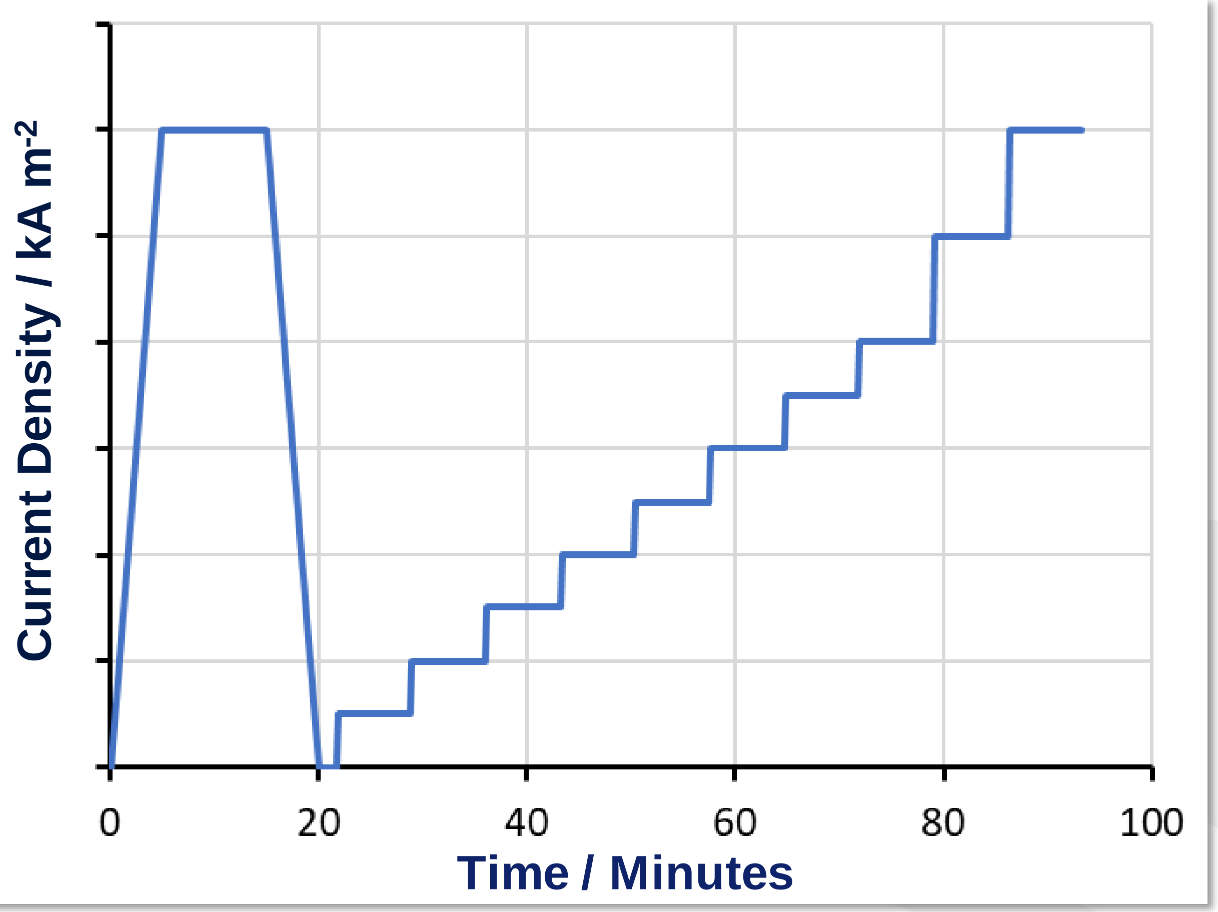
CHLORCOAT™ Coating Development

New Cathode Development

Mini-cell tests using CHLORCOAT cathodes

- F8081 membrane (AGC)
- CHLORCOAT anode
- 29.3% caustic feed (~32% exit)
- 300gpl alkaline brine feed (~200gpl exit)
- 85°C cell temperature



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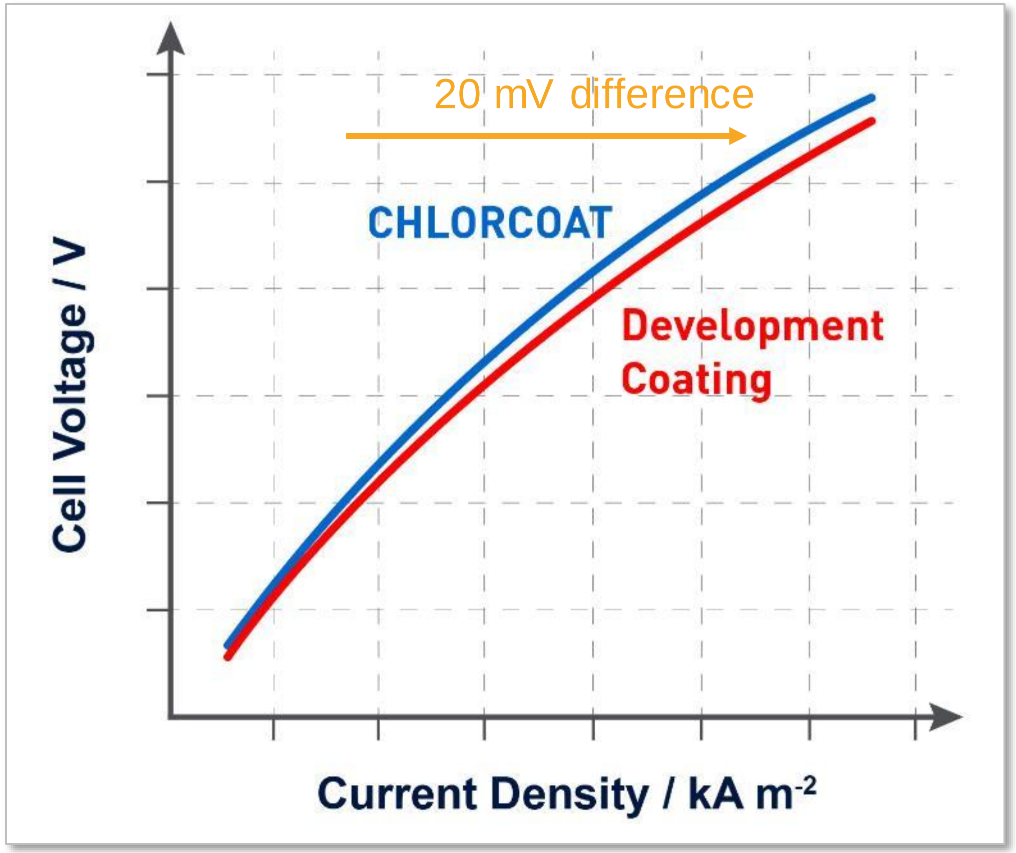
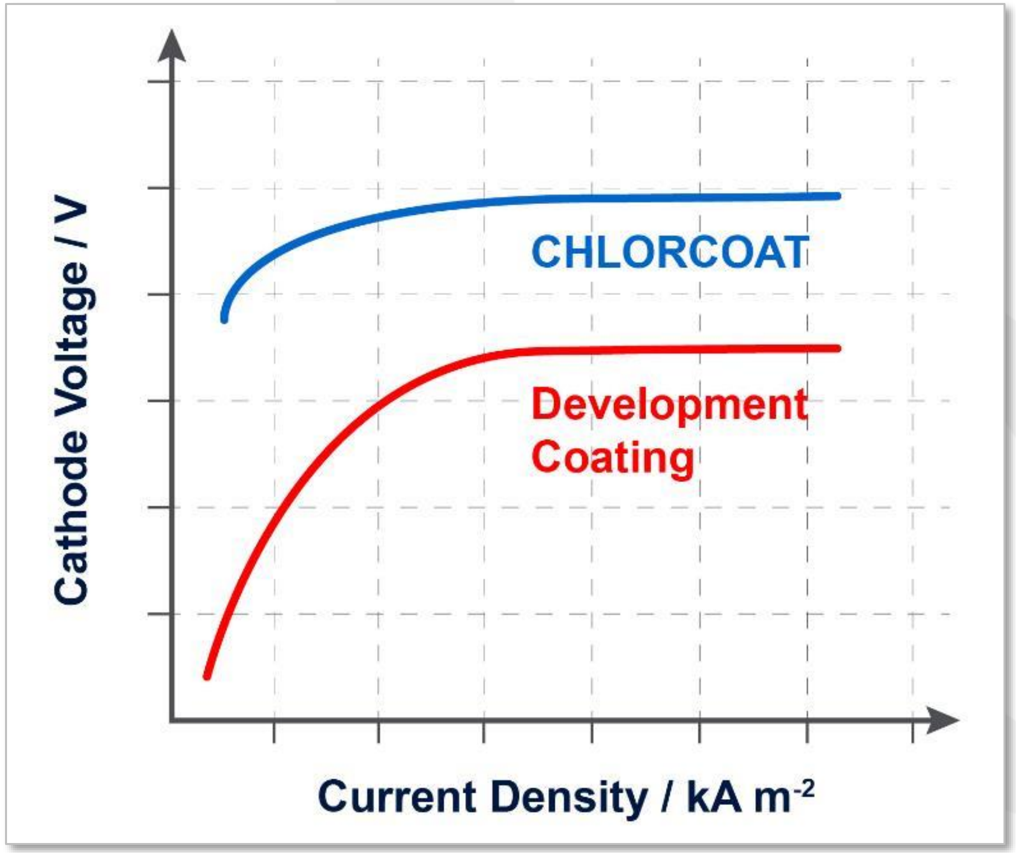
Initial Polarisation

Just after cell start up, Development Coating has 15-20mV benefit vs. CHLORCOAT at 6kA/m^2

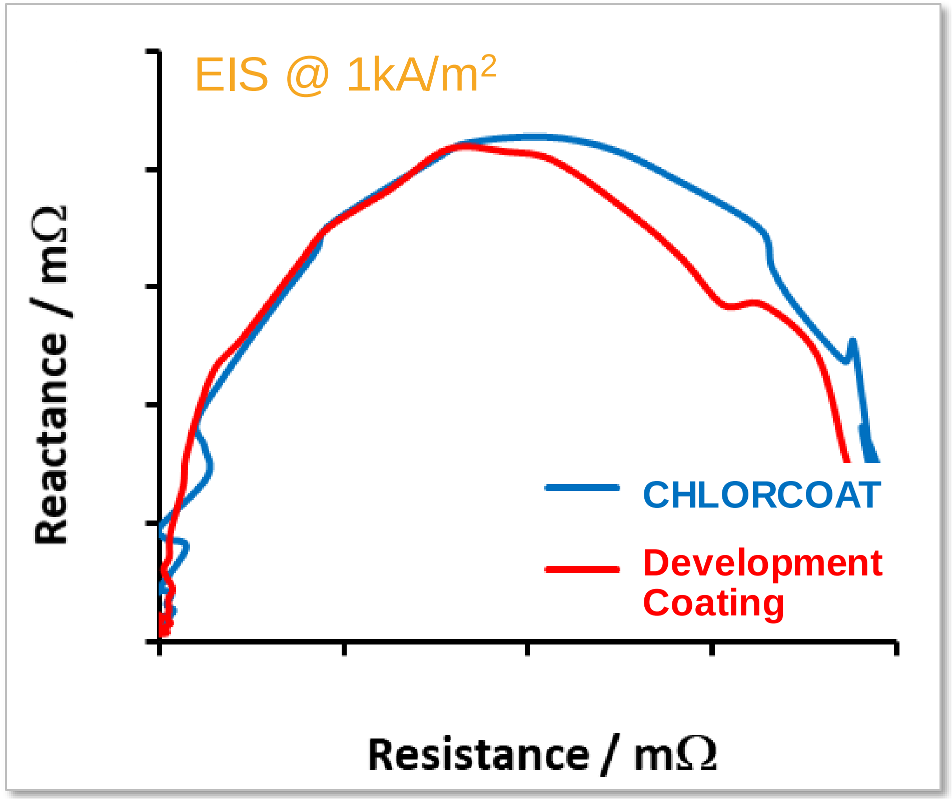


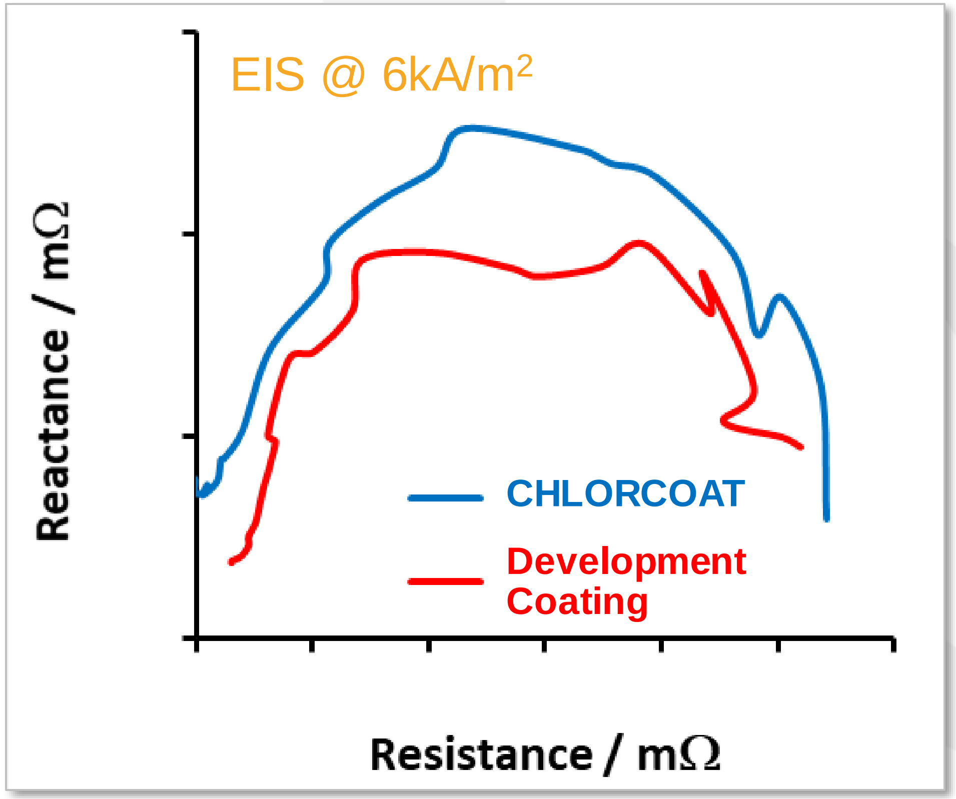


Initial Polarisation

Electrochemical impedance spectroscopy verifies better performing cathode

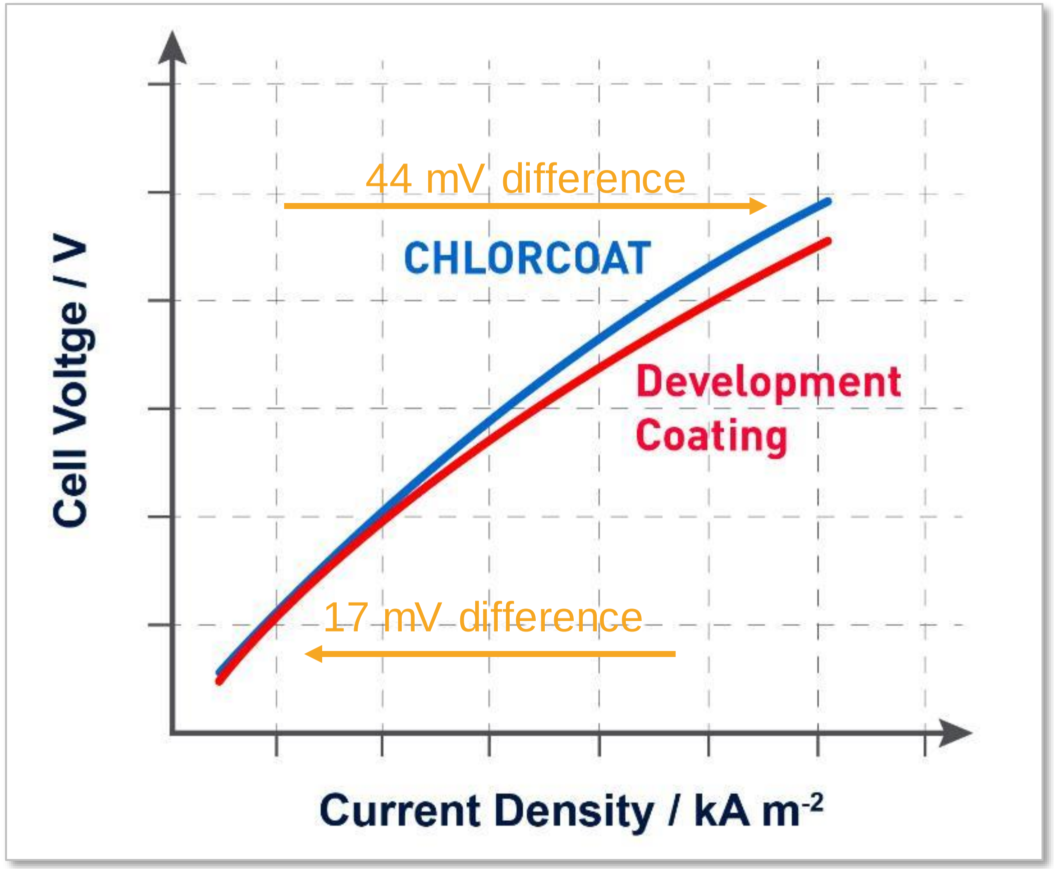
- CHLORCOAT arc is wider implying slower kinetics than Development Coating

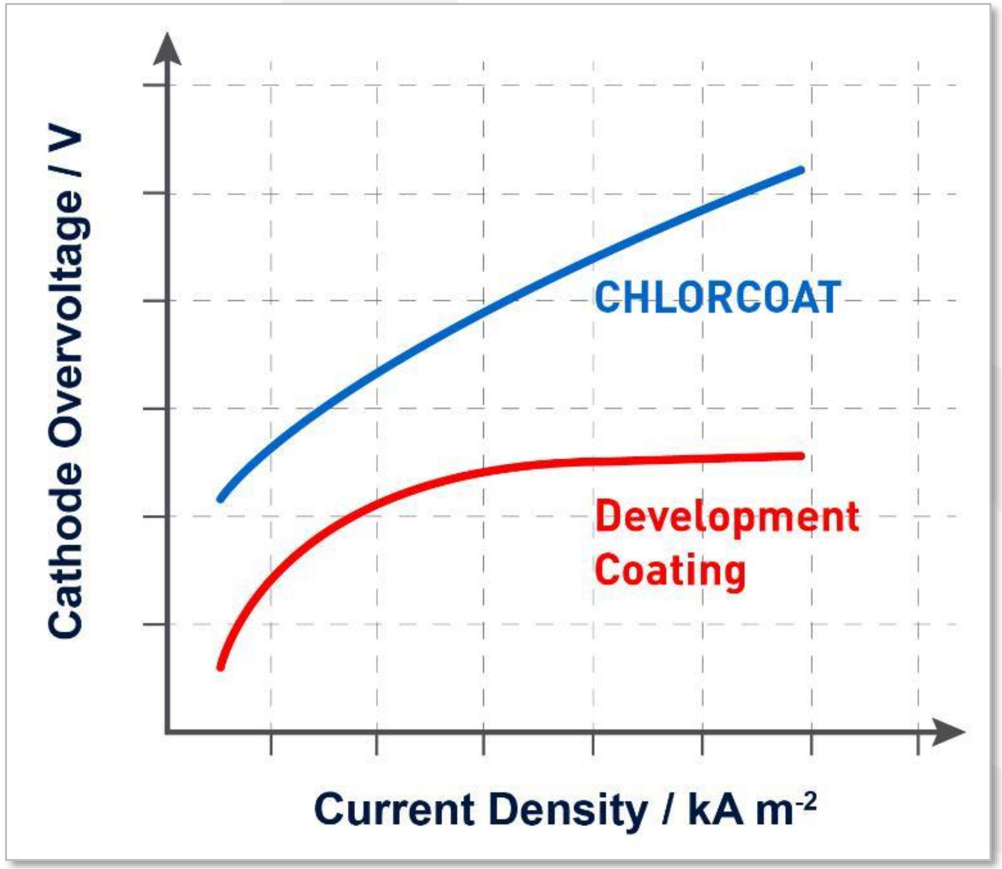




Final Polarisation

After 24 hours at 6kA/m^2, Development Coating has 30-40mV benefit vs. CHLORCOAT at 6kA/m^2





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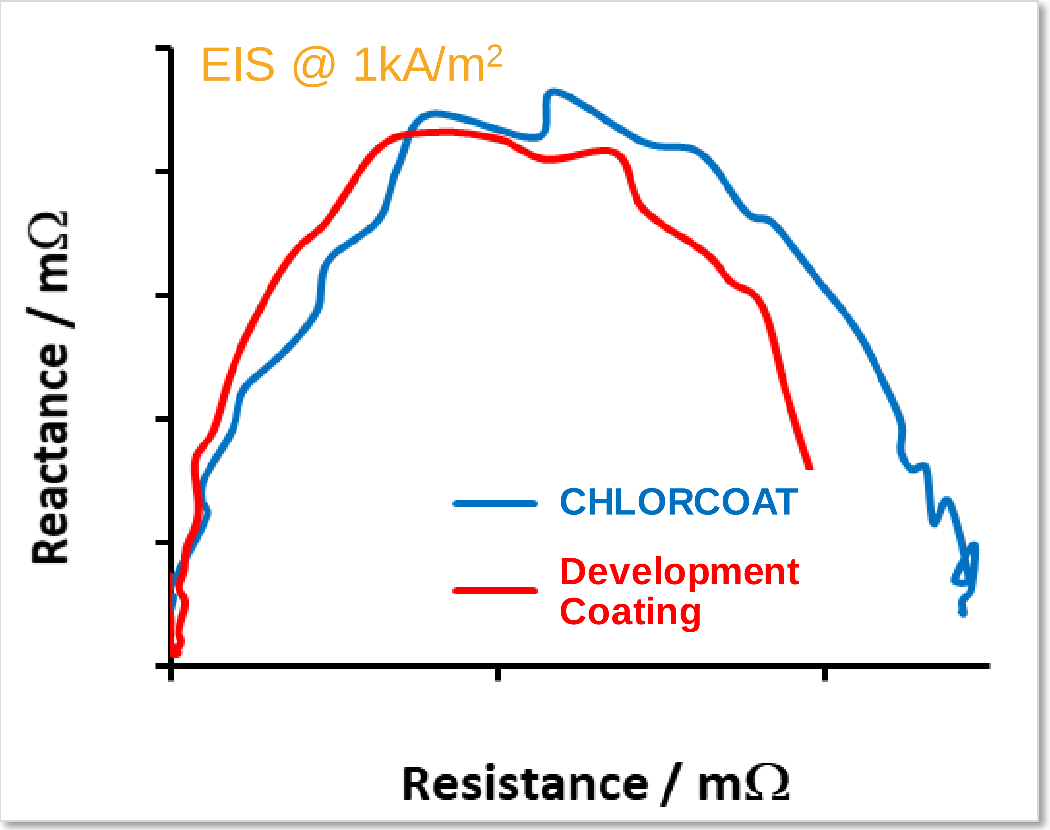
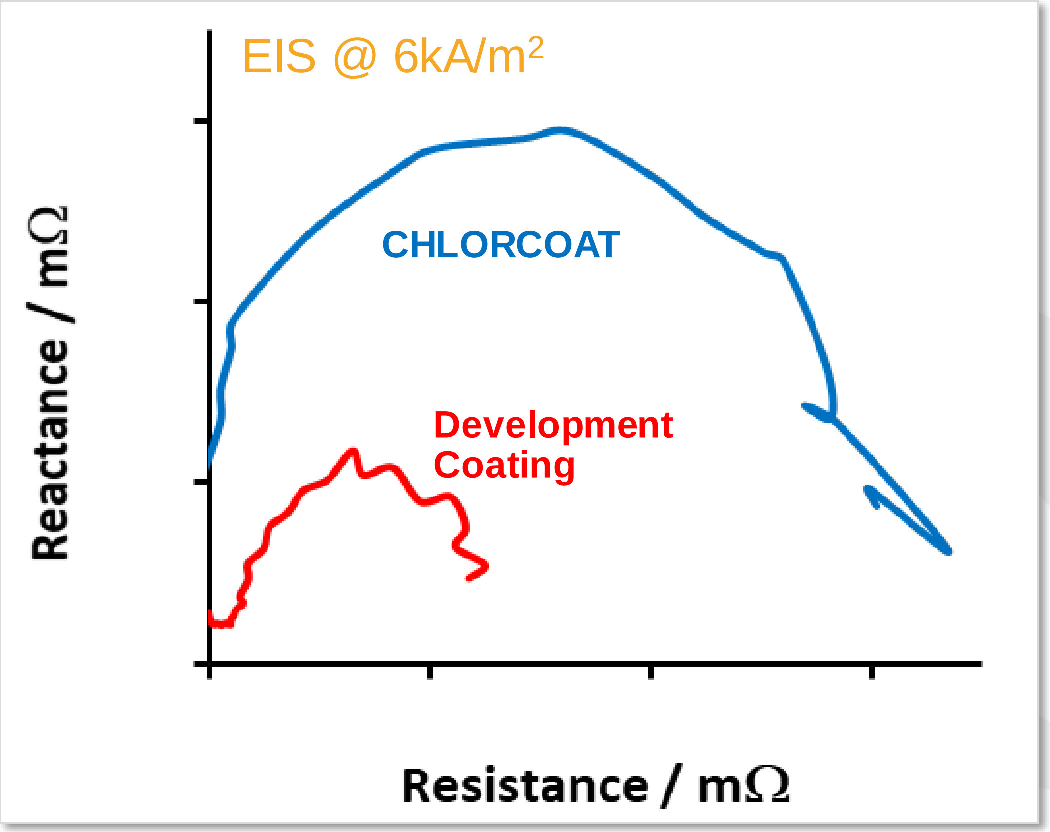
Final Polarisation

Electrochemical impedance spectroscopy verifies much better performing cathode

- CHLORCOAT arc is much wider and taller implying slower kinetics than Development Coating

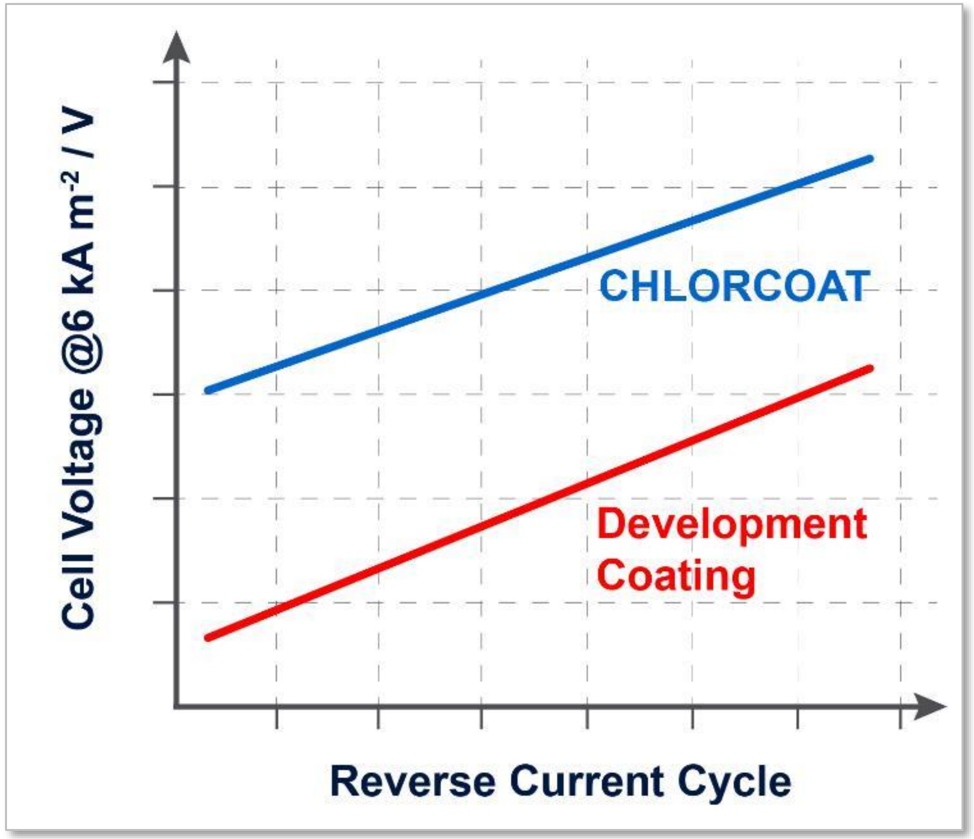


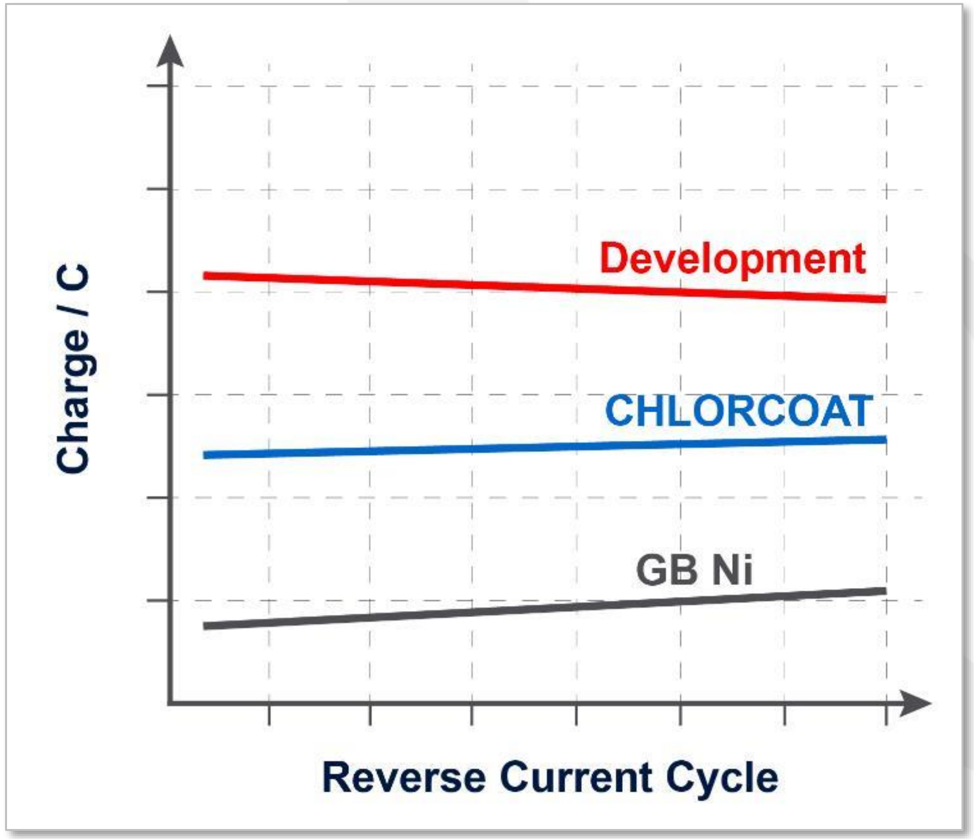


Reverse Current Tolerance

Both cathodes appear to have a similar tolerance to reverse current

- Development Coating maintains it performance benefit vs. CHLORCOAT





Research Innovation - Summary

INEOS mini-cell testing capabilities are a major boost to electrode coating research and development

- Enhanced experimentation
- Exceptional control
- Fundamental insights
- Agile experimental techniques enables us to deliver tangible savings for operators
  - Results suggest ~20mV benefit on start-up and ~40mV benefit after stabilisation

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Key Takeaways

Key Takeaways

INEOS lead the way in advanced chlor-alkali research and development

- Our innovations in mini-cell experimentation allow us to deliver electrolyser performance gains
- As operators ourselves, we hold additional unique capabilities and research insights

Our BICHLOR™ electrolysers deliver superior energy performance

- Featuring a class leading output of **69,000 MTPA NaOH** per electrolyser** and less than **1990* kWh/te NaOH** @ 6kA/m^2 power consumption
- Our agile research techniques will improve this impressive performance further!

All operators can benefit from CHLORCOAT™ with our module coating & refurbishment services

- Facilities dedicated to the refurbishment of all types of membrane electrolyser electrode
- Including repair and coating of electrodes, flanges, coated mesh and feed tubes

* Expected value @ 385mbarg Cl_2, 90°C and 32wt% NaOH **Based on 350 days operation and 7kA/m^2

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Acknowledgements

New Coatings Team, INEOS Electrochemical Solutions

- Daniel Korwin-Kochanowski
- Elizabeth Farrand-Edwards
- Laura Mawdsley
- Martin Hogarth
- Amy Colleran
- Sam Jones

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Q & A :
We welcome any questions you have.

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