

Effect of Water on Cu Electrodeposition from Ethaline Deep Eutectic Solvent

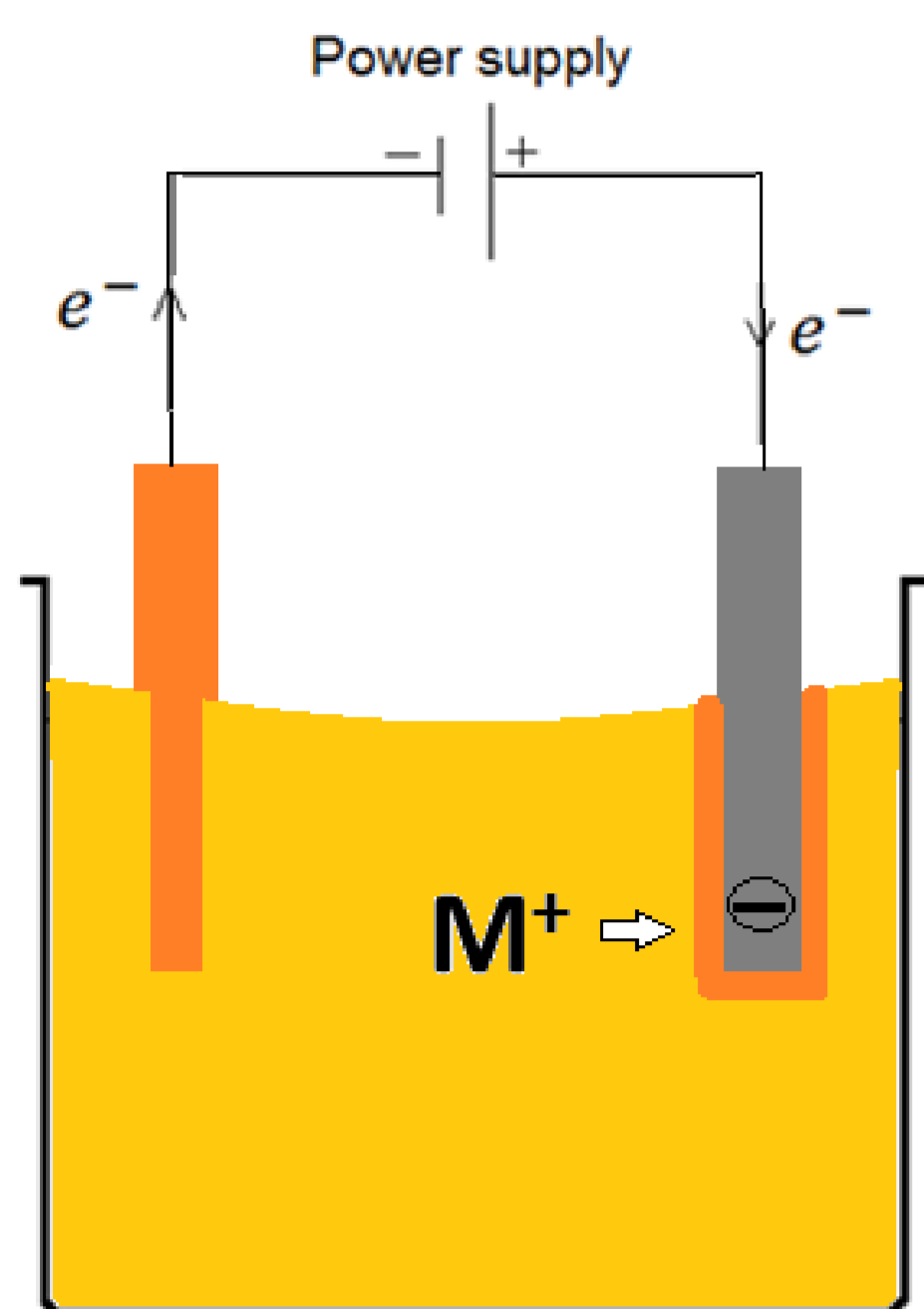
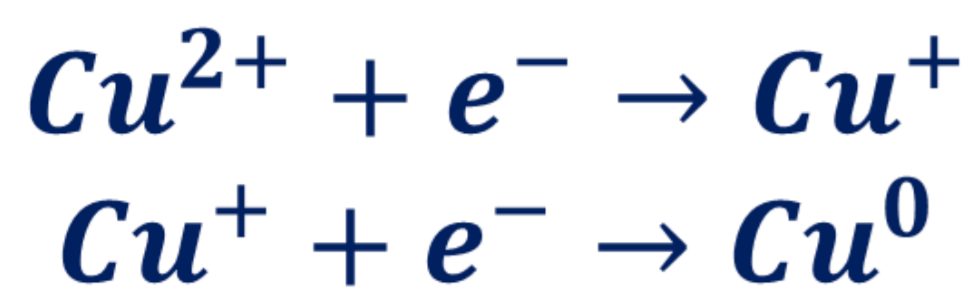
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Introduction

Electrodeposition



Ionic Liquids

Chloroaluminate ionic liquids

- ❖ Water sensitive

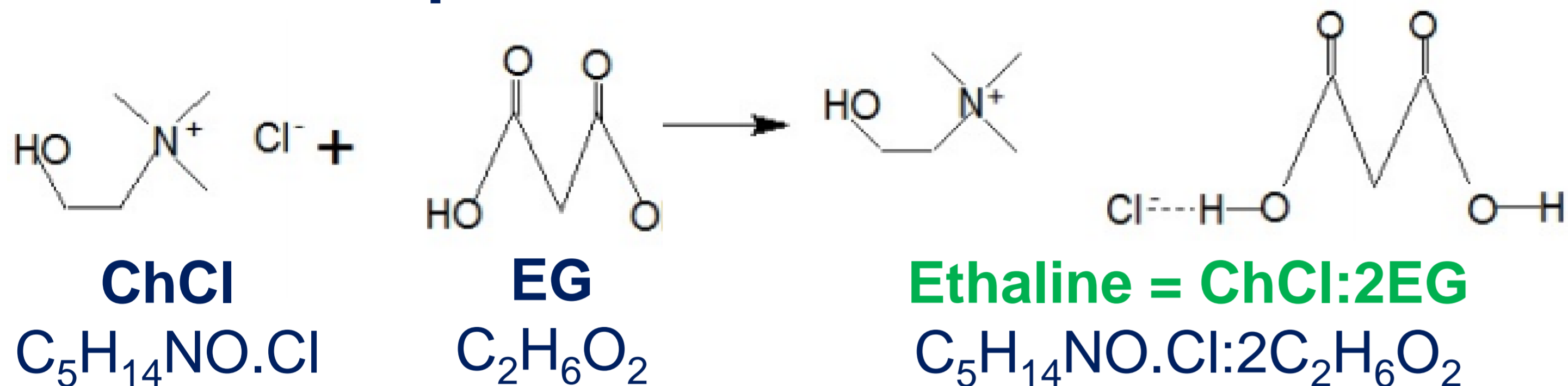
Non-chloroaluminate ionic liquids

- ❖ Costly

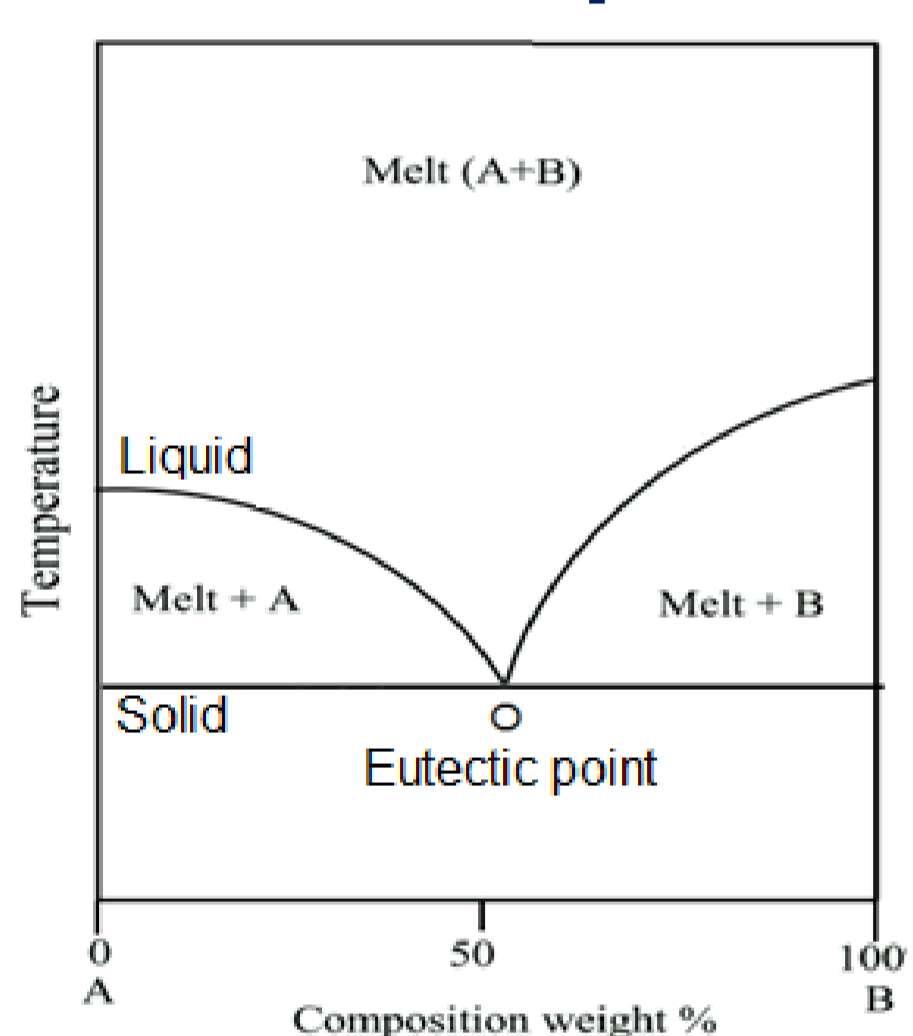
Deep eutectic solvents

- ❖ Stable (water tolerant)
- ❖ Reasonable cost
- ❖ May be exploitable at large scale

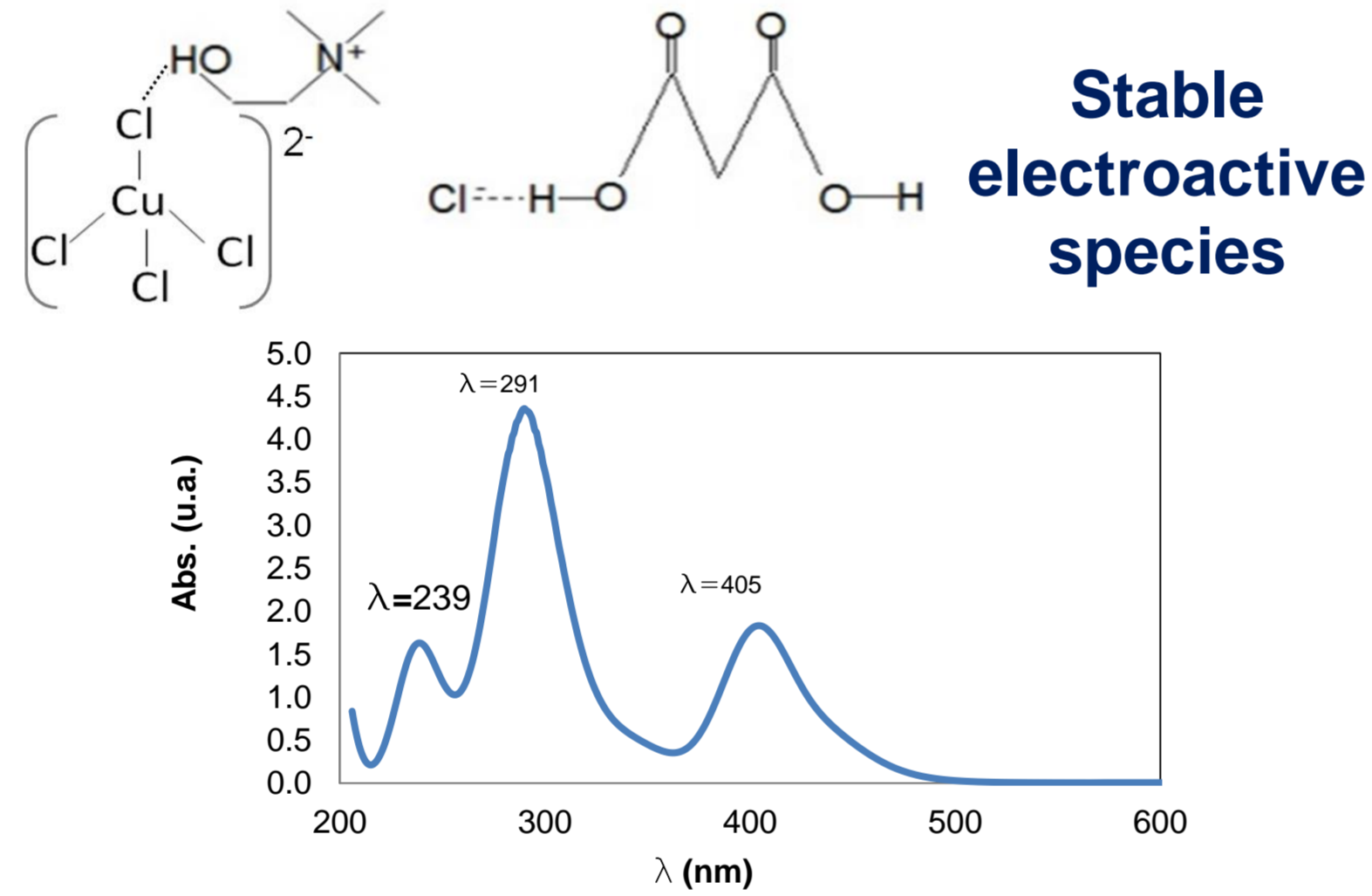
Deep eutectic solvent: Ethaline



Eutectic point



Speciation of Cu in ethaline



Importance of the study

Historically, **metal electrodeposition** from ionic liquids were carried out from dry systems. However, **ethaline is a hygroscopic substance**; therefore, the effect of H₂O on Cu deposition needs to be understood.

Research questions

- ❖ What is the ability of the electrolyte to uptake water?
- ❖ What is the effect of water on the physical properties and on the electrochemical behaviour of the electrolyte?
- ❖ Does water improve or deteriorate the characteristics of Cu deposits?

Conclusions

- ❖ The absorption rate of H₂O of the electrolyte with cupric chloride salt was 0.42 wt%/day.
- ❖ The limiting currents of the process are increased with high water concentrations, which is explained by the capacity of H₂O to reduce viscosity and promote the diffusivity of Cu²⁺ ions in the solution.
- ❖ The uniformity of Cu deposits is deteriorated with increasing H₂O content.

Experimental

1. Karl Fischer titration to determine water content

- ❖ In ethaline w/o 0.2 M CuCl₂·2H₂O.
- ❖ In the electrolyte that was exposed to the air over 4 weeks.

2. Physical properties at differing water content

- ❖ Conductivity
- ❖ Viscosity
- ❖ Density

3. Electrochemical behaviour: Influence of water on limiting current

- ❖ RDE experiments in a divided electrochemical cell using Pt as WE and CE and a Ag wire as RE.

T= 25 °C
Rotation speed: 700 rpm.

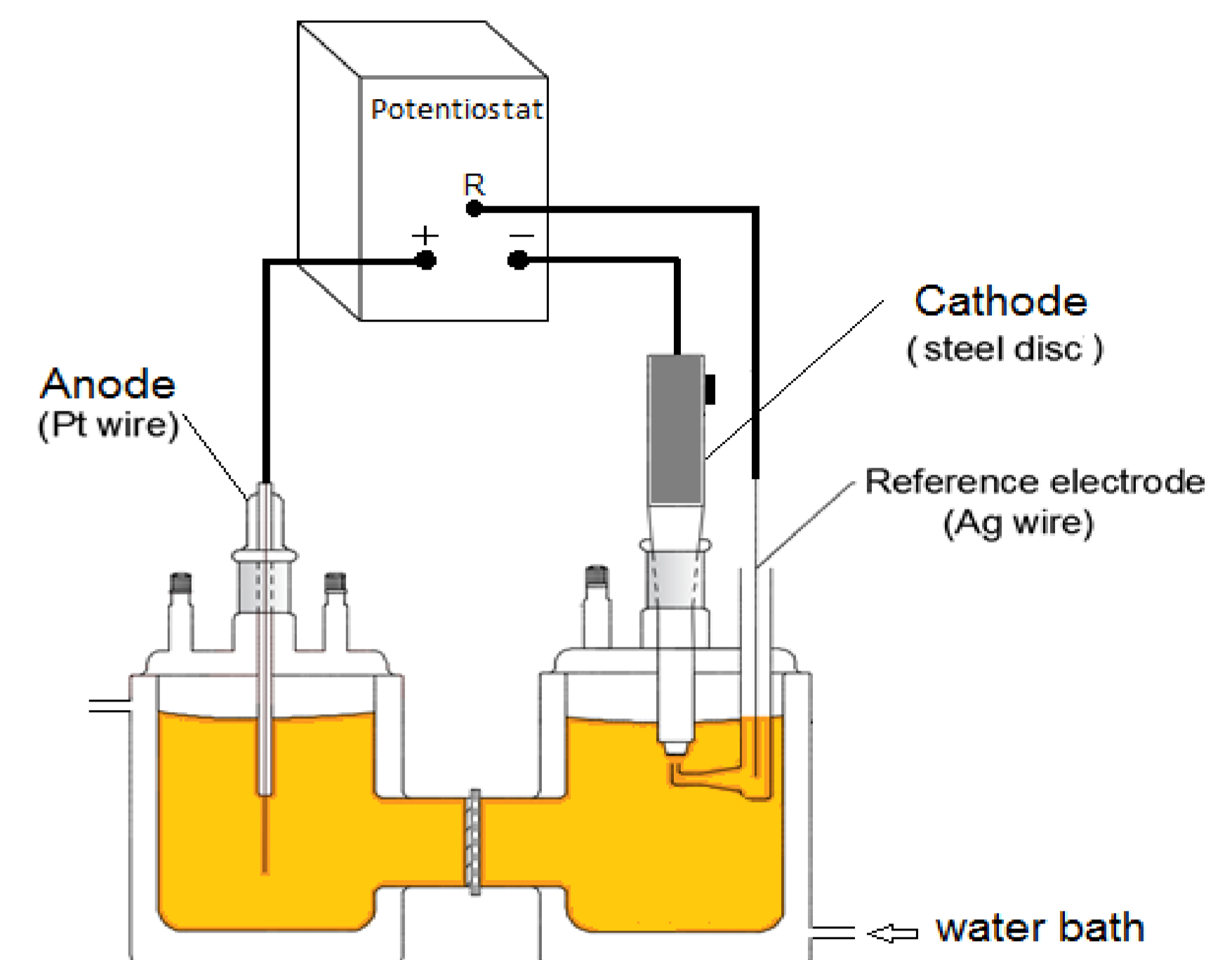
4. Electrodeposition experiments at differing water content

- ❖ Water was added gradually to the electrolyte.
- ❖ The spiked water was the same moisture adsorbed by the electrolyte over 4 weeks.

Electrolyte	Water content (wt%)
Ethaline melt with 0.2 M CuCl ₂ ·2H ₂ O	1 st week
	2 nd week
	3 rd week
	4 th week

5. Deposit characterisation

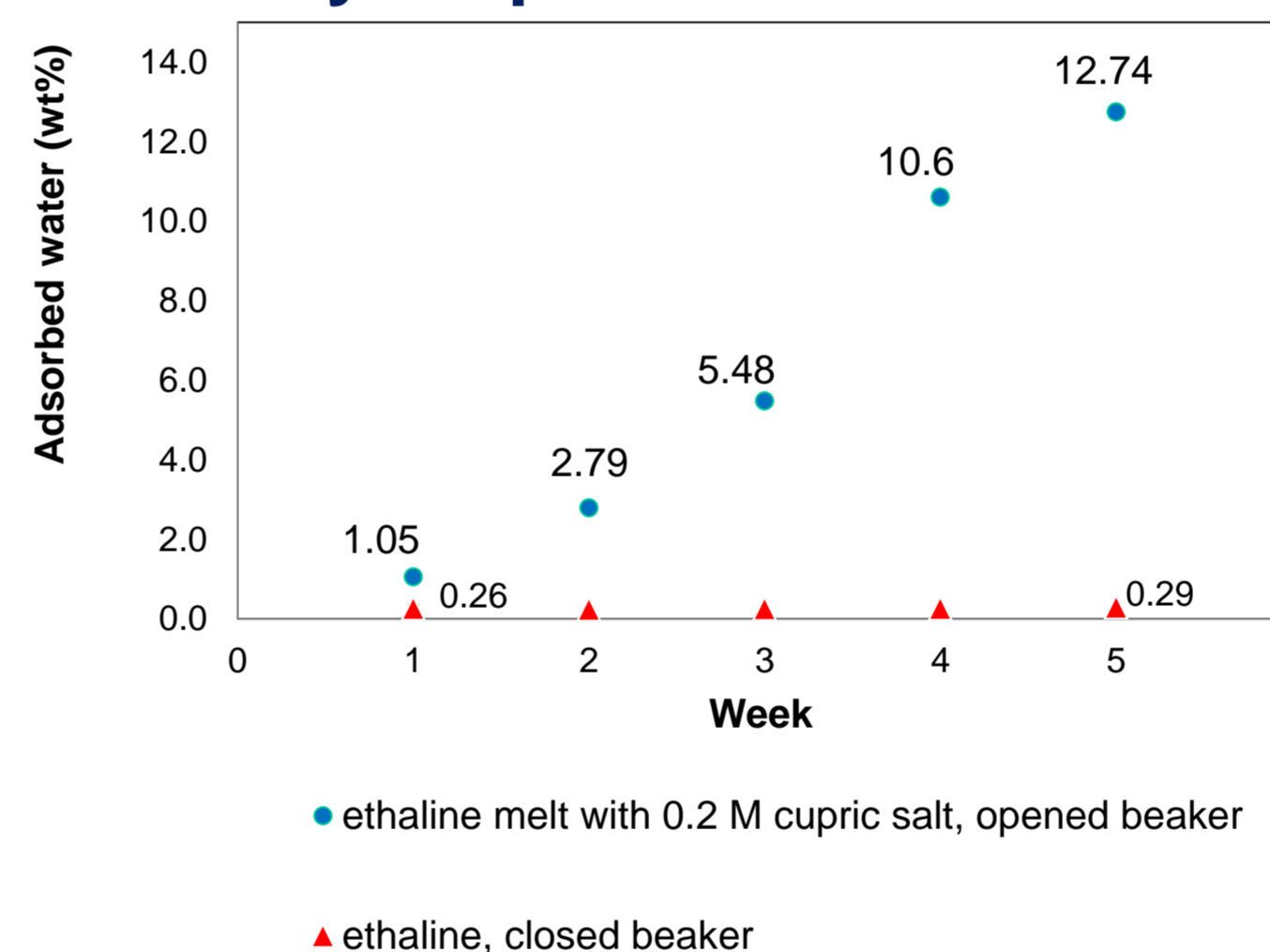
- ❖ Morphology: Hitachi SU6600 SEM.
- ❖ Purity of deposits: Oxford Inca 350 X-Max detector.



- ❑ Galvanostatic plating
- ❑ Operating current= 80% i_{Lim}
- ❑ t= 7200 s, WE= steel disc

Results & Discussion

Electrolyte uptake of water with time



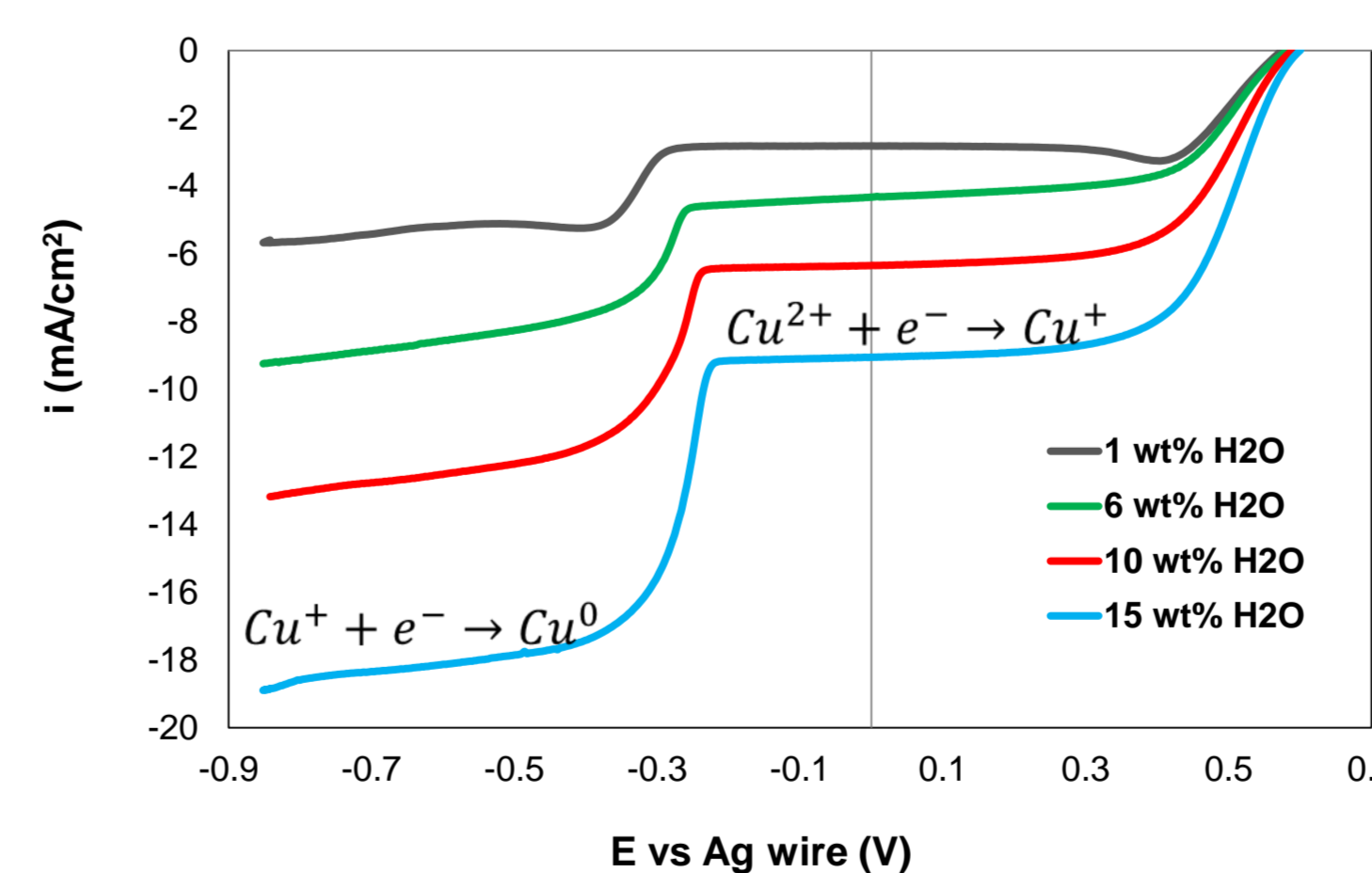
Effect of water on physical properties

Water content (wt%)	η (cP)	κ (mS/cm)	ρ (g/cm ³)
3	0.044	0.009	1.13
6	0.034	0.010	1.12
10	0.022	0.012	1.12
15	0.015	0.015	1.11

Effect of water on morphology

WC (wt%)	Morphology		Purity (%)
	Center	Edge	
1	i = 3.84 mA/cm ²	i = 5.3 mA/cm ²	96
6	i = 4.84 mA/cm ²	i = 8.2 mA/cm ²	97
10	i = 7.04 mA/cm ²	i = 12.1 mA/cm ²	99
15	i = 9.8 mA/cm ²	i = 18.5 mA/cm ²	99

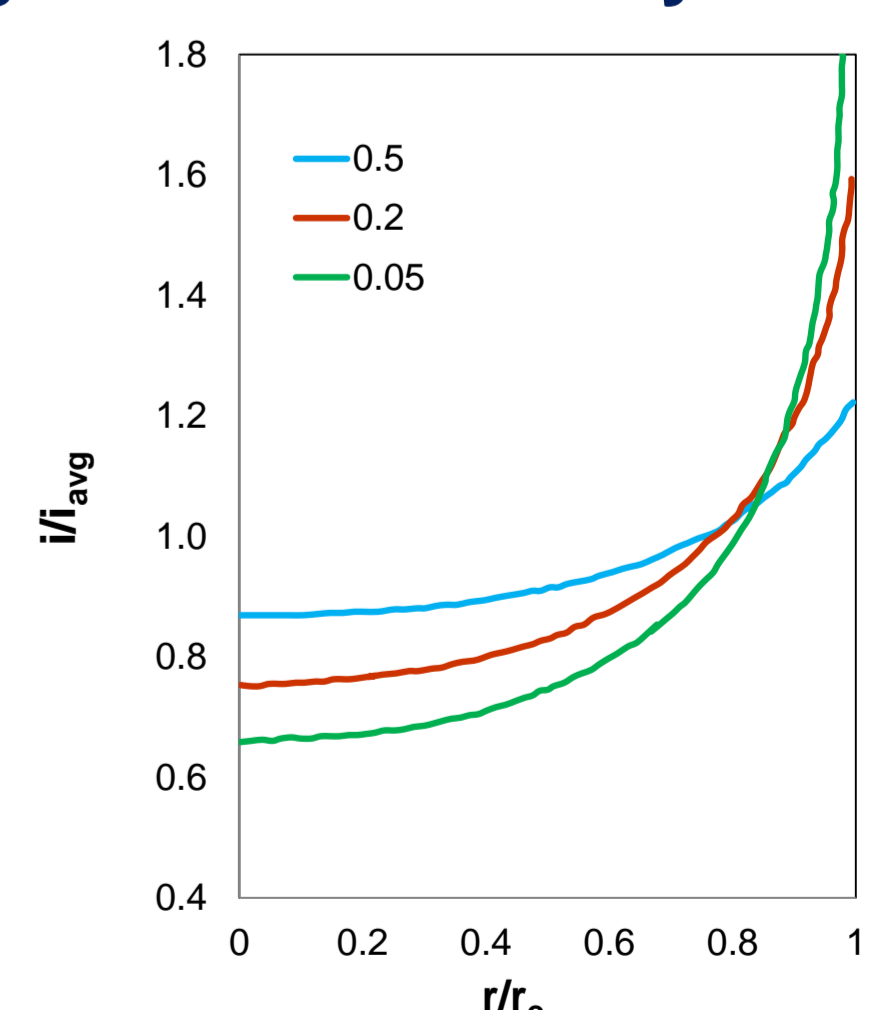
Effect of water on Cu electrochemical behaviour



Uniformity: Wagner number analysis

$$Wa_T = \frac{RT \kappa}{a_c F i_{avg} r_o}$$

WC (wt%)	α	Wa _T
3	0.18	0.38
6	0.27	0.25
10	0.26	0.21
15	0.44	0.10



Acknowledgements