Chromium electrodeposition using a novel type IV deep eutectic solvent

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Summary

A novel Deep Eutectic Solvent (DES) can be formed between $CrCl_3{\cdot}6H_2O$ and urea. This system can be used for electrochemical applications, such as electrodeposition. The physical properties of these systems have been characterised and it was noted that their viscosities were lower and the conductivities were found to be larger than for other reported DES systems.[1,2] Energy dispersive X-ray spectroscopy (EDX) analysis and hardness tests showed that this system could be used for hard chrome deposition. It has been shown that these systems are excellent candidates for electrochemical applications.

Why is chromium electrodeposition important?

- Protect the material against corrosion.
- Improve the surface properties.
- Achieve optimum decorative effects.

Deep Eutectic Solvents

- DESs are a type of ionic liquid composed of an organic cation and an organic/inorganic anion.[1]
- A novel Type IV DES can be formed from $CrCl_3{\cdot}6H_2O$ and urea, *i.e.* no need for an organic cation (Fig 1).
- There are four types of DESs (Fig 2).

Fig 1: The new DES and its two solid components.

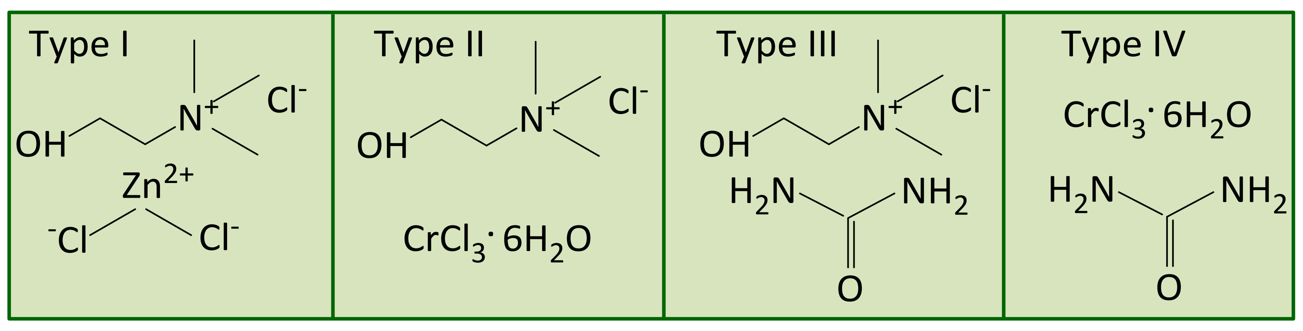


Fig 2: The four different types of DESs.

Issues with aqueous solutions

- Low current efficiencies.
- Hydrogen evolution during plating.
- Low thermal stability.
- Evaporation of solution.

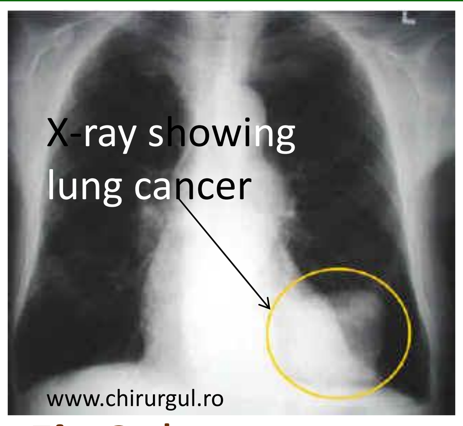


Fig 3: lung cancer.

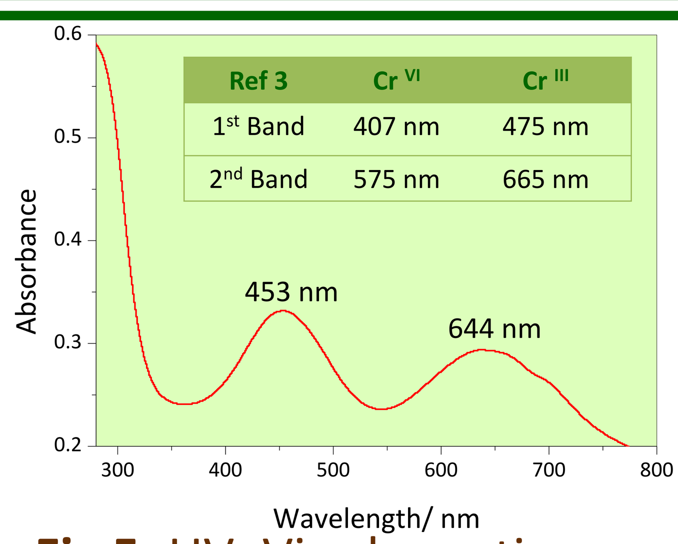
Issues with chromium VI

- Inhalation of Cr^{VI} causes lung cancer (Fig 3).
- Highly toxic.
- Can cause allergic reactions and asthma.
- Highly corrosive (Fig 4).

Fig 4: Cr^{VI}: highly corrosive.

UV-Vis spectroscopy

- Two bands exist in acid media for both Cr^{VI} and Cr^{III} complexes[3] (Fig 5 inset).
- Two absorbance bands observed in the new system correspond to the Cr^{III} band regions (Fig 5).



Ref 3	Cr^{VI}	Cr^{III}
1st Band	407 nm	475 nm
2nd Band	575 nm	665 nm

Fig 5: UV–Vis absorption spectra.

The Physical Properties

- These liquids have attractive physical properties (Fig 6), are easy to synthesize and relatively inexpensive.
- We have shown that these are excellent candidates for electrochemical applications that avoid using Cr^{VI} and its compounds, which are toxic and classified as carcinogenic.[4]

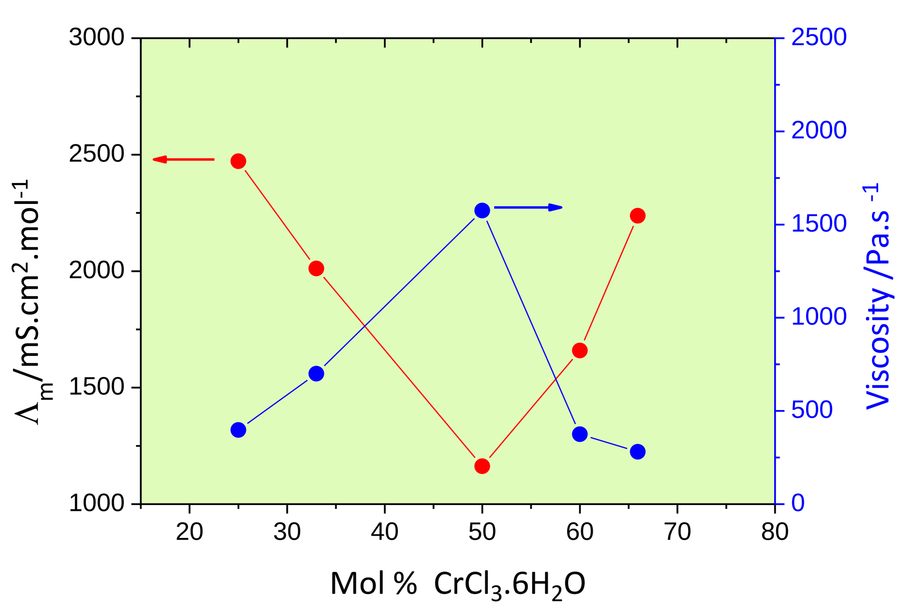


Fig 6: Molar conductivity vs. viscosity of urea / $CrCl_3{\cdot}6H_2O$ as a function of temperature and compositions

The chemical structures

- The eutectic composition for this solvent is ~67% $CrCl_3{\cdot}6H_2O$ (Fig 7) and~33% urea (Fig 8).
- This composition has the lowest freezing point (Fig 9).

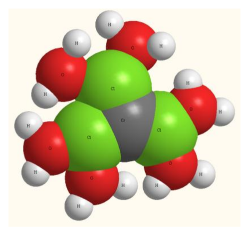


Fig 7: $CrCl_3{\cdot}6H_2O$

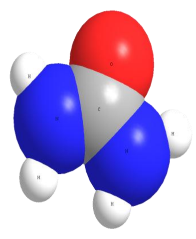


Fig 8: Urea

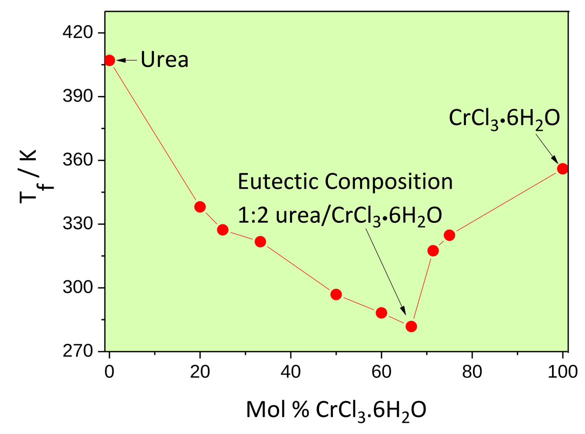


Fig 9: The phase diagram of the system

Chromium electrodeposition

- Hull cell experiments (Fig 10) were carried out to deposit a metal over a range of current densities at a constant voltage.
- These results emphasise that these systems could be excellent candidates for chromium plating application.

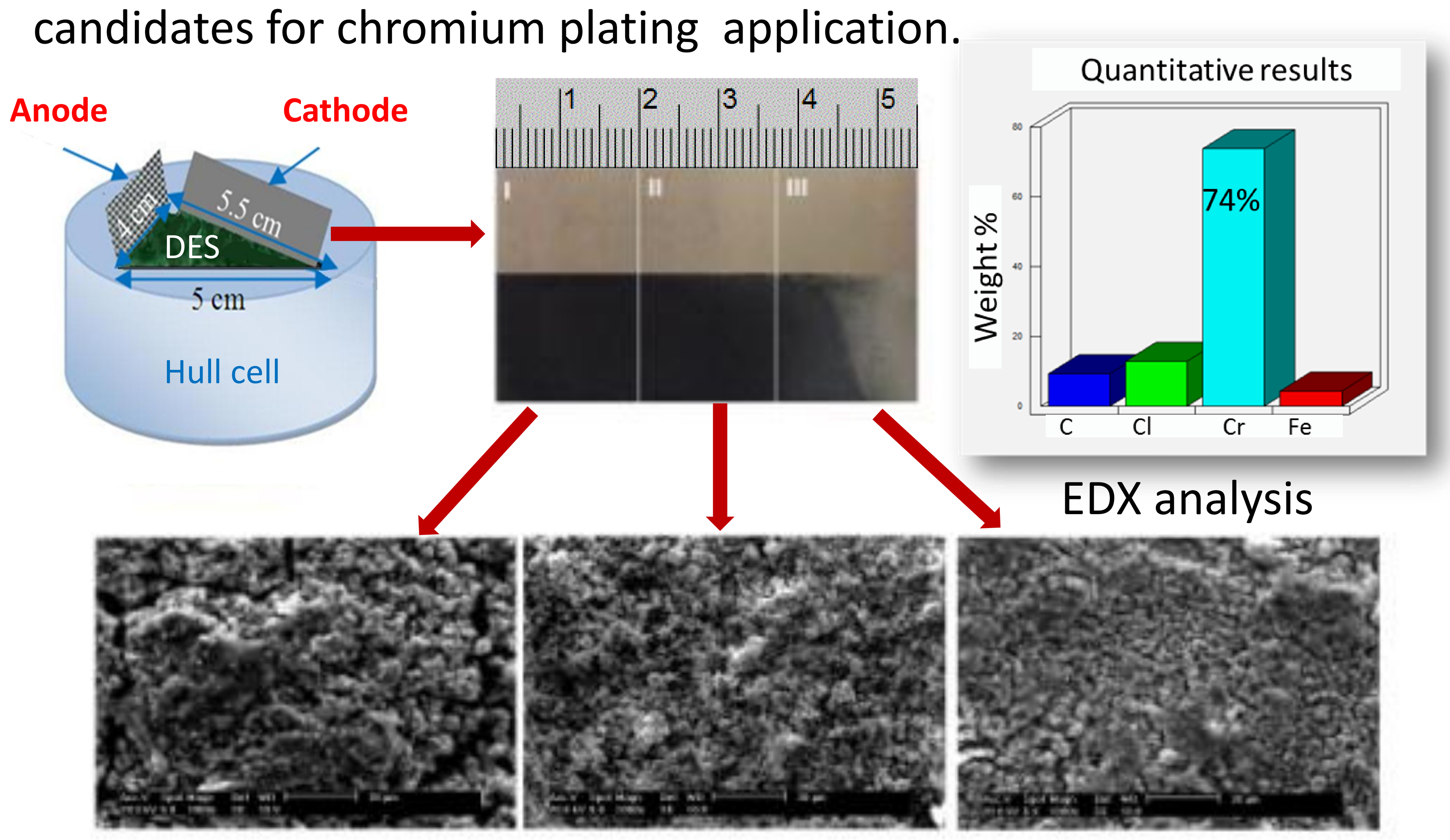


Fig 10: Bulk deposition from the 1:2 urea/ $CrCl_3{\cdot}6H_2O$ system at 40 °C for 1 hour onto a mild steel electrode at a current density of 0.2 mA/cm^2 resulted in an amorphous black deposit of ~65 µm thicknesses.

Coating thickness and hardness analysis

- The average thickness was ~65µm (Fig 11) for the highest current density section from the Hull cell test.
- Average hardness was ~600 HV0.5 (Fig 12)

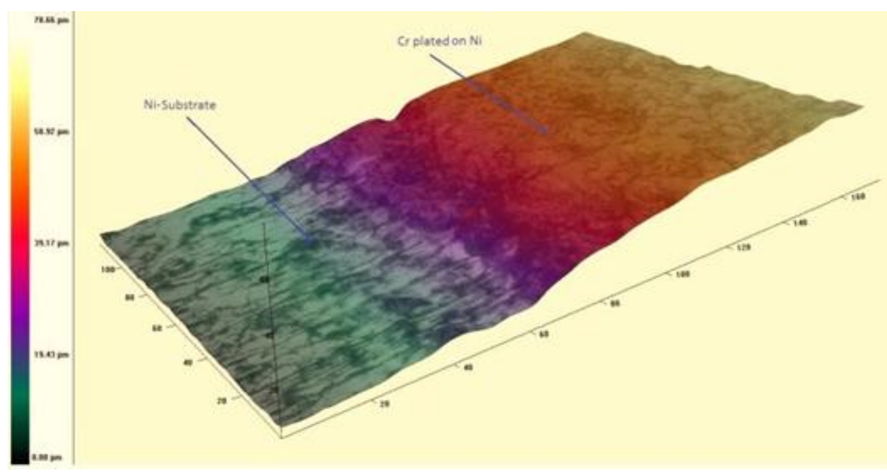


Fig 11: Surface morphology

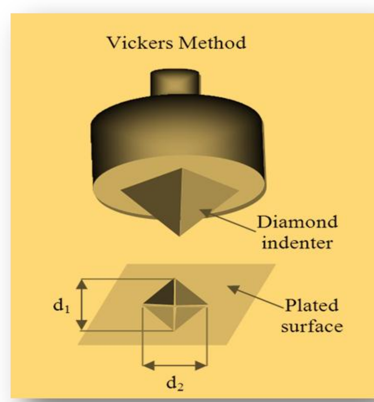


Fig 12: Hardness test

Conclusion

- A chromium plating liquid with higher fluidity than previously seen for other chromium containing DES systems[2] has been formed.
- Avoids use of Cr^{VI} and its compounds, which are toxic.
- Large surface tension and density values similar to other DESs were obtained for this system .
- A range of deposit morphologies can be obtained from this system, suggesting that these liquids are suitable candidates for hard chromium electrodeposition.

Current efficiency

The current efficiency of this new process was found to be in excess of 74%, which is much higher than the current aqueous chromic acid process (up to 20%).

References

[1] A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chemical Communications*, 2003, 70-71.
[2] A. P. Abbott, G. Capper, D. L. Davies and R. K. Rasheed, *Chem. Eur. J.*, 2004, 10, 3769-3774.
[3] P. J. Elving, and B. Zemel, J. Amer. Chem. Soc., 1957,79, 1281-1285.
[4] C. T. J. Low, R. G. A. Wills and F. C. Walsh, Surface and Coatings Technology, 2006, 201, 371-383.