Process Optimization of a Greener Chromium Electroplating System using Cr(III)-Ethaline Deep Eutectic Solvent

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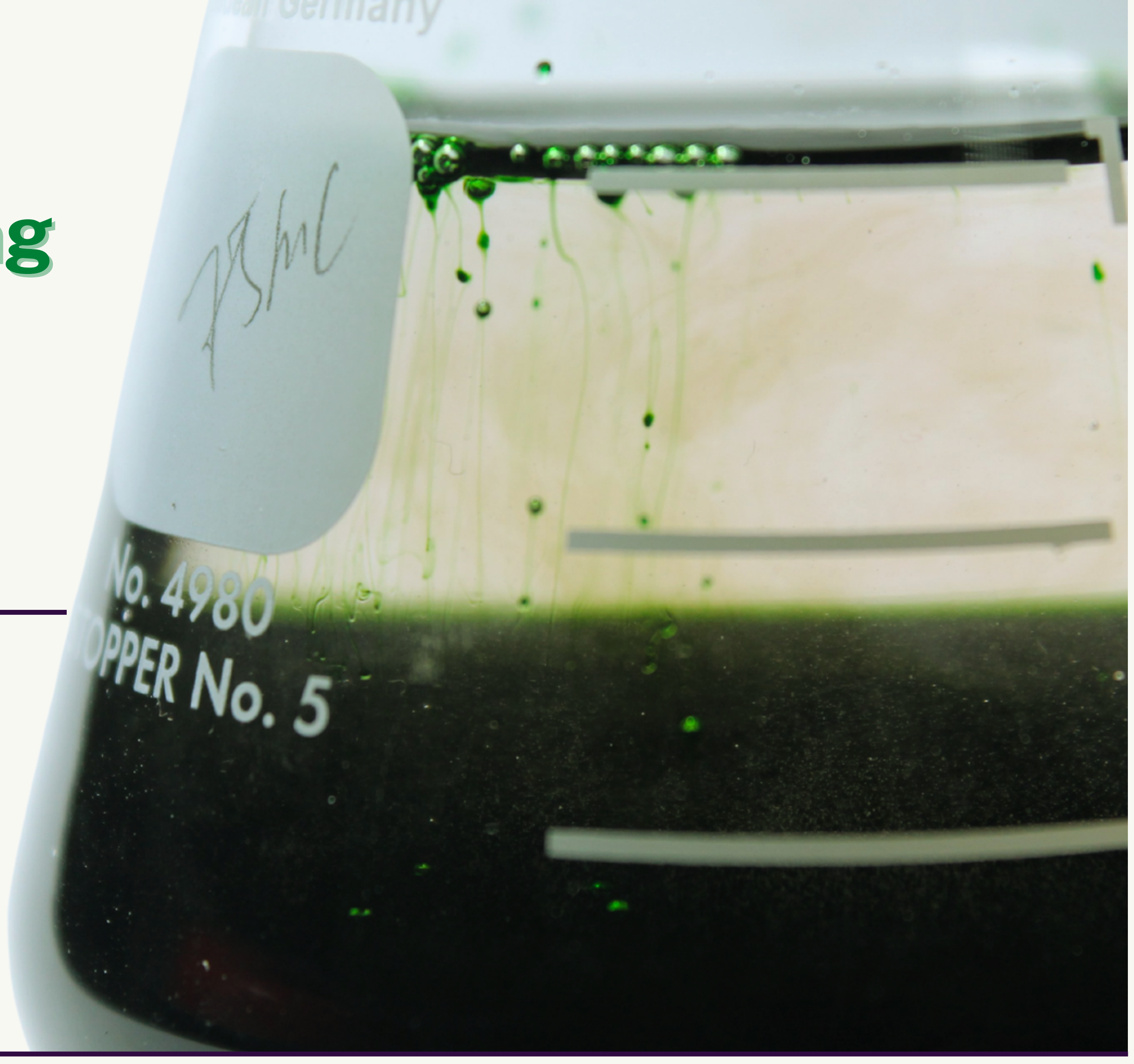


Abstract

In this study, Box-Behnken response surface methodology was employed as the optimization tool to determine the desired settings for three parameters that were investigated – Cr concentration, plating potential, and plating temperature. The response variables were viscosity, conductivity, plating efficiency, and Knoop hardness (HK). A two-electrode cell composed of a Ni-plated brass cathode and SS304 anode with a DC power supply was used to deposit chromium from the prepared electrolytes. As a result, the analysis showed that the plating system can reach 20-40% plating efficiency, and Cr deposits with 300-1000 HK value. The optimized setting was determined to be at 132 g/L Cr concentration, 1.45 V plating potential, and 40 oC temperature, and has a predicted viscosity value of 28.3 mPa-s, conductivity reading of 13.9 mS/cm, 30% plating efficiency, and 966 HK value.

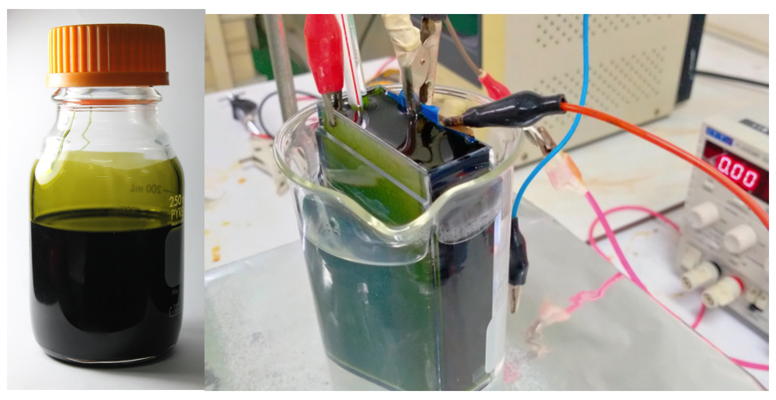
Introduction

The need to develop a new chromium plating system that is safer, cleaner, utilizes Cr(III) salt and non-aqueous system emerges. In this context, non-aqueous electrolytes such as ionic liquids demonstrated a promising alternative to this concern. Ionic liquids, particularly deep eutectic solvents, are simply ionic materials that are liquid at room temperature and known to have ionic character, non-volatile, wide electrochemical window, and are more environmentally accepted than traditional aqueous plating baths.

Objective

This study presents preliminary results in developing a sustainable trivalent chromium plating system. Chromium plating from deep eutectic solvent-based electrolytes had already showed promising potentials as supported from the collected data from published papers. This study takes a step to optimize a process recipe for a target application.

Methodology



Box-Behnken response surface methodology was employed as the optimization tool using Minitab software

Investigated Parameters	Settings	Response Parameters
Chromium concentration	140 g/L 100 g/L 60 g/L	*Viscosity*
Plating Potential	1.45 V 1.60 V 1.75 V	*Conductivity* *Plating Efficiency (%)*
Plating Temperature	30 C 35 C 40 C	*Knoop Hardness (HK)*

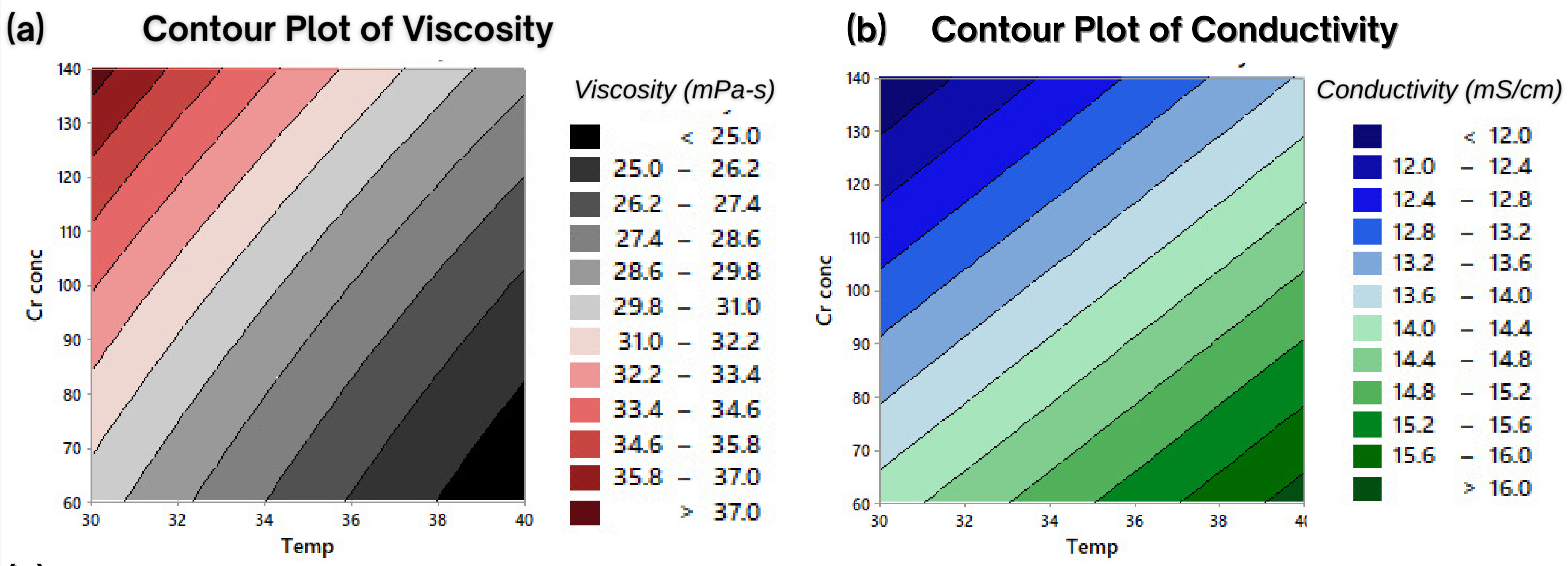
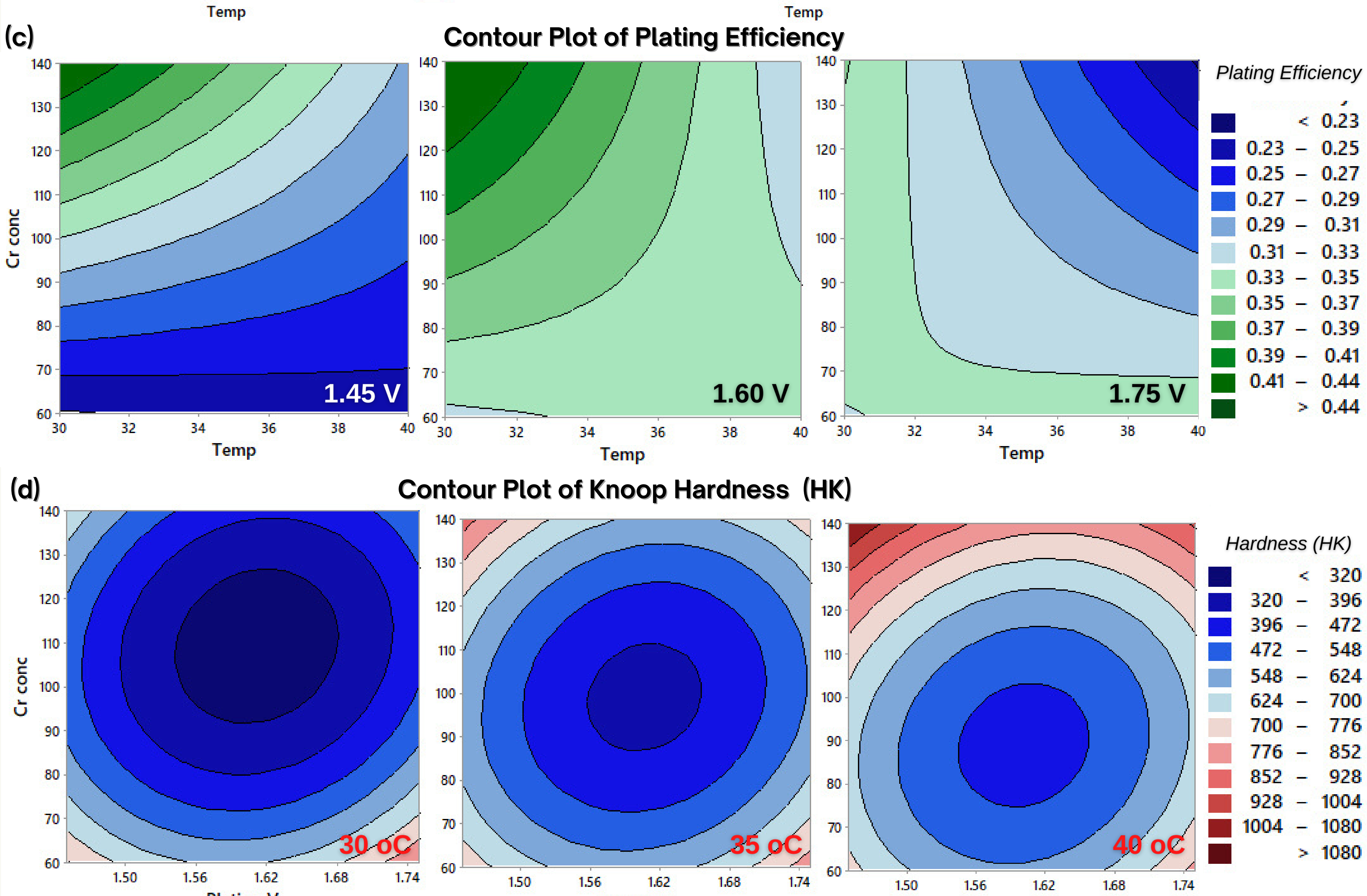


Figure 1 (a-d) Summary of the contour plots obtained from the response surface methodology analysis for (a) viscosity, (b) conductivity, (c) plating efficiency, and (d) Knoop hardness values.



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- Protsenko, V. S., Bobrova, L. S., Kityk, A. A. & Danilov, F. I. (2020) Kinetics of Cr (III) ions discharge in solutions based on a deep eutectic solvent (ethaline): Effect of water addition. J. Electroanal. Chem. 864, 114086.

Results and Discussion

Effects of the Investigated Parameters on the Responses

The independent factors affecting conductivity and viscosity were Cr concentration and plating temperature. The contour plot of viscosity (Fig 1a) showed that it decreases with decreasing Cr concentration and increasing plating temperature. The opposite trend was observed for conductivity (Fig 1b) which increases with decreasing Cr concentration and increasing temperature.

Plating efficiency (PE) was found to be affected by all investigated factors. The trends observed (Fig 1c) were that increasing Cr concentration and decreasing plating temperature promotes better efficiency. The presence of more Cr source can deposit more material, while electroplating at lower temperature prevents the participation of water electrolysis that lowers the plating efficiency. In terms of the effects of the plating potential, plating efficiency reached a plateau near 1.6 V as this is the potential at the limiting current density.

Hardness highly relies on the structure and composition of the deposit and was also found to be affected by all the investigated factors. The hardness value was noticed to have dips occurring near 90-110 g/L Cr concentration, and 1.55-1.6 V plating potential. These dips are consequences of the structure and composition of the deposits obtained from these parameters.

Optimization Results

The response optimizer was utilized using Minitab software to acquire the optimized settings. The optimization was based on viscosity (minimum), conductivity (maximum), plating efficiency (target: 30%), and Knoop hardness (maximum). A desirability of 0.795 was achieved with the following optimized settings: 132 g/L Cr concentration, 1.45 V plating potential, and 40 oC temperature. The optimized formulation has predicted viscosity value of 28.3 mPa-s, conductivity reading of 13.9 mS/cm, 30% plating efficiency, and 966 HK value

Conclusion

The study was able to obtain an optimal setting for chromium electroplating using the Box-Behnken response surface methodology. The optimized setting was determined to be 132 g/L Cr concentration, 1.45 V plating potential, and 40 oC temperature, and has a predicted viscosity value of 28.3 mPa-s, conductivity reading of 13.9 mS/cm, 30% plating efficiency, and 966 HK value. The results obtained can be a starting step for the development of Cr(III)-ethaline plating system with plating additives for the ultimate goal of a safer, cleaner, and more sustainable Cr electroplating process.

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