【Grant-in-Aid for Scientific Research (S)】

Broad Section D

Title of Project： **Analysis, Design, and Construction of Highly Concentrated Electrolytes for Innovative Electrodeposition Technologie**

MURASE Kuniaki

(Kyoto University, Graduate School of Engineering, Professor)

Research Project Number: 20H05663 Researcher Number：30283633

Keyword：Electrodeposition, Concentrated solutions, Solution chemistry, Metal complexes, Metallographic structure

【Purpose and Background of the Research】

Electrodeposition (ED) that uses electrochemical reduction of metal ion species in electrolytes to form metals and alloys is an elemental technology for various industrial processes. We recently developed novel ED technologies that utilize a series of highly concentrated electrolytes (HCEs) for, for example, environmentally friendly trivalent chromium plating, ED of aluminum for battery anodes, and formation of Cu_2O semiconductor layers for photovoltaics. These HCEs provide environments depleted of free solvent molecules, and we believe that metal complexes that are stable only in such special environments control the ED behaviors and the resulting deposits. However, their details are still unclear.

In this study, we will look deeper into the metal complexes formed specifically in HCEs and, at the same time, investigate the metallography and physical properties of the electrodeposits to get comprehensive understanding of the new ED processes (Fig. 1).

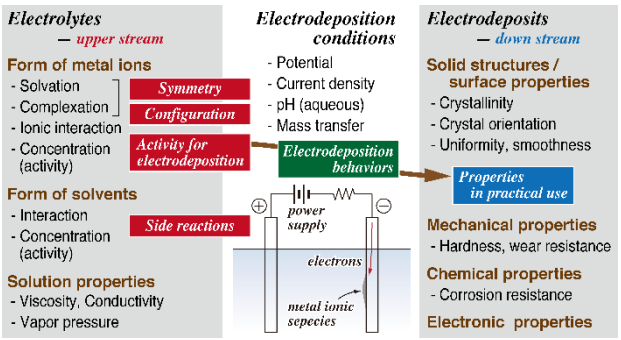

Figure 1 Possible governing factors in ED process

【Research Methods】

This study includes three subjects: (*i*) environmentally friendly electroplating using hydrate melts, (*ii*) ED of Al using glyme-based deep eutectic solvents, and (*iii*) ED of Cu_2O layers using aqueous electrolytes of concentrated α-hydroxyl acids. Co-investigators are Prof. UMEBAYASHI Yasuhiro (Niigata University) and Prof. NAKANO Hiroaki (Kyushu University). The analysis of dissolved species in the electrolytes is performed using vibrational spectroscopy (Raman, FT-IR), UV-visible spectroscopy, nuclear magnetic resonance, and mass spectrometry. Computational chemistry, *e.g.* MO and MD calculations, is employed in addition to the multivariate analysis of the spectra. Crystallographic features of the deposits are analyzed by a variety of electron microscopy techniques (SEM, TEM, EBSD). The data on mechanical, chemical, and electronic properties will also be collected.

【Expected Research Achievements and Scientific Significance】

The HCEs give a new class of solution system different from general aqueous solutions or ionic liquids. The data on the complexes therein, *i.e.* chemical structure (Fig. 2) and their thermodynamics, and on the correlation among the complexes, ED behaviors, and resulting deposits will help us to design HCEs to obtain more sophisticated materials in terms of practical use.

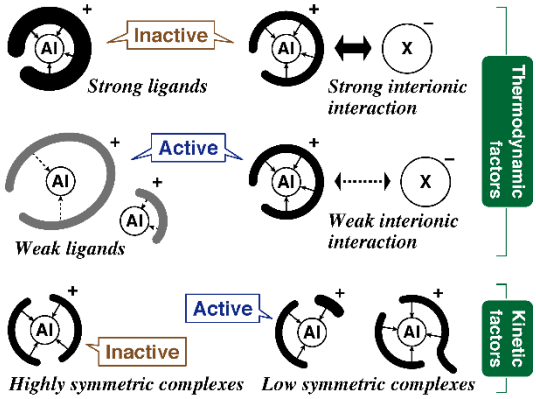

Figure 2 Possible relationship between Al complex in the electrolyte and the resulting ED behavior.

【Publications Relevant to the Project】

- K. Adachi, A. Kitada, K. Fukami, K. Murase, Crystalline Chromium Electroplating with High Current Efficiency Using Chloride Hydrate Melt-based Trivalent Chromium Baths, *Electrochim. Acta*, **338**, 135873/1-8 (2020).
- A. Kitada, K. Nakamura, K. Fukami, K. Murase, Electrochemically Active Species in Aluminum Electrodeposition Baths of $AlCl_3$/Glyme Solutions, *Electrochim. Acta*, **211**, 561-567 (2016).

【Term of Project】 FY2020-2024

【Budget Allocation】 153,000 Thousand Yen

【Homepage Address and Other Contact Information】

http://www.echem.mtl.kyoto-u.ac.jp