

LiAlCl₄-NaAlCl₄-NaAlBr₄-KAlCl₄: a Low-Melting Molten Salt Mixture for the Electrodeposition of Aluminum

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Aluminum is an excellent corrosion-resistant coating for ferrous metals. It is well established that the corrosion resistance of Al is derived from the spontaneous formation of a thin, protective layer of oxide. Furthermore, this barrier oxide film is usually “self-repairing” unless the metal is exposed to an environment containing strong alkalis or halide salts, which can penetrate and/or destroy the oxide layer and induce corrosion. There are a number of very successful commercial processes for electroplating Al. These processes can be subdivided into two general categories: those based on mixtures of AlX₃ + LiAlH₄ dissolved in ether solvents and those that are based on mixtures of trialkylaluminum compounds and halide salts dissolved in aromatic hydrocarbon solvents. The obvious safety concerns associated with these volatile, pyrophoric plating baths has led to the exploration of haloaluminate ionic liquids as replacement baths. In fact, the first demonstrated use of such ionic liquids for this purpose dates to seminal work carried out with AlCl₃ + ethylpyridinium bromide in 1948.¹ Since that time, there have been numerous reports describing the electroplating of Al from room-temperature chloroaluminate ionic liquids based on AlCl₃ + 1-alkylpyridinium or 1,3-dialkylimidazolium chloride salts, as well as from higher melting chloroaluminate molten salts, e.g., AlCl₃ + NaCl.

In this poster, we describe the electrodeposition of Al from a complex mixture of inorganic haloaluminate salts first described by Hjuler, et al.,² LiAlCl₄-NaAlCl₄-NaAlBr₄-KAlCl₄ (3:2:3:2) [or LiAlBr₄-NaAlCl₄-KAlCl₄ (3:5:2)]. This Lewis neutral molten salt mixture melts at 86 °C and can therefore be classified as an *inorganic ionic liquid*. It was originally formulated for use as an electrolyte for rechargeable Al/molten salt/Ni₃S₂ batteries. As Figure 1 illustrates, the specific conductance of this ionic liquid is considerably higher than that of organic chloroaluminate ionic liquids, such as AlCl₃ + 1-ethyl-3-methylimidazolium chloride (EtMeImCl), and only slightly less than that of the higher melting, binary AlCl₃ + NaCl system. Furthermore, the LiAlCl₄-NaAlCl₄-NaAlBr₄-KAlCl₄ ionic liquid offers a number of advantages over existing Al plating systems. First, this electrolyte system is completely inorganic, is not based on pyrophoric additives or volatile organic solvents, and is environmentally friendly. Second, the components are relatively inexpensive compared to organic chloroaluminate ionic liquids based on 1,3-dialkylimidazolium chloride salts such as EtMeImCl and require less effort for purification. Finally, Al films prepared in this inorganic ionic liquid should exhibit less internal stress as a result of the lower plating temperature compared to those prepared in high temperature (~175 °C) inorganic systems such as AlCl₃-NaCl.

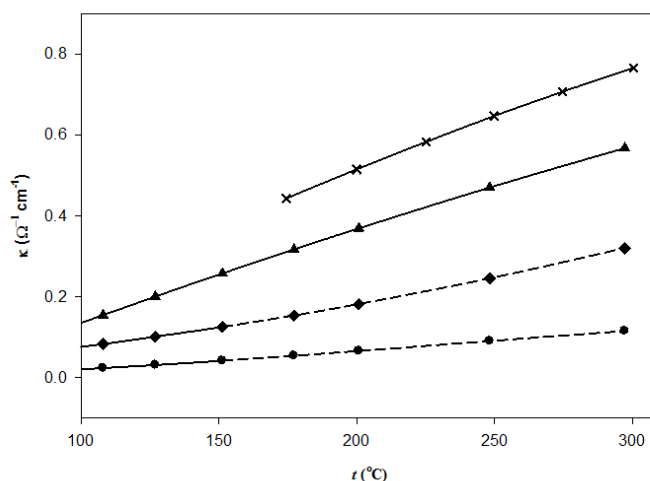


Figure 1: Specific conductivity as a function of temperature for (x) AlCl₃-NaCl (1:1),³ (▲) LiAlCl₄-NaAlCl₄-NaAlBr₄-KAlCl₄ (3:2:3:2),² (◆) AlCl₃-EtMeImCl (1:1),⁴ and (●) BuMepyroTf₂N.⁵ The dotted lines represent extrapolated data.

¹F. H. Hurley, U.S. Pat. 2,446,331 (1948).

²H. A. Hjuler, S. von Winbush, R. W. Berg, and N. J. Bjerrum, *J. Electrochem. Soc.*, **136**, 901-906 (1989).

³H. A. Hjuler, R. W. Berg, K. Zachariassen, and N. J. Bjerrum, *J. Chem. Eng. Data*, **30**, 203-211 (1985).

⁴A. A. Fannin, Jr., D. A. Floreani, L. A. King, J. S. Landers, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes, and J. L. Williams, *J. Phys. Chem.*, **88**, 2614-2621 (1984).

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