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MOLTEN2024

Thermodynamic Modeling of Species Distribution in $AlCl_3$:BMIC Salts

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1 INTRODUCTION

➢Ionic liquids (ILs) are organic salts that contain organic cations and either organic or inorganic anions with melting points less than 100°C.

➢Among them, 1-butyl-3-methylimidazolium chloride (BMIC), when combined with aluminum chloride ($AlCl_3$), shows great promise in fields like batteries and low-temperature aluminum electrodeposition.

➢This study discusses the thermodynamic modeled species concentration profile of the $AlCl_3$:BMIC ionic liquid electrolyte with its electrical conductivity, and average cathode current density during the aluminum electrochemical process.

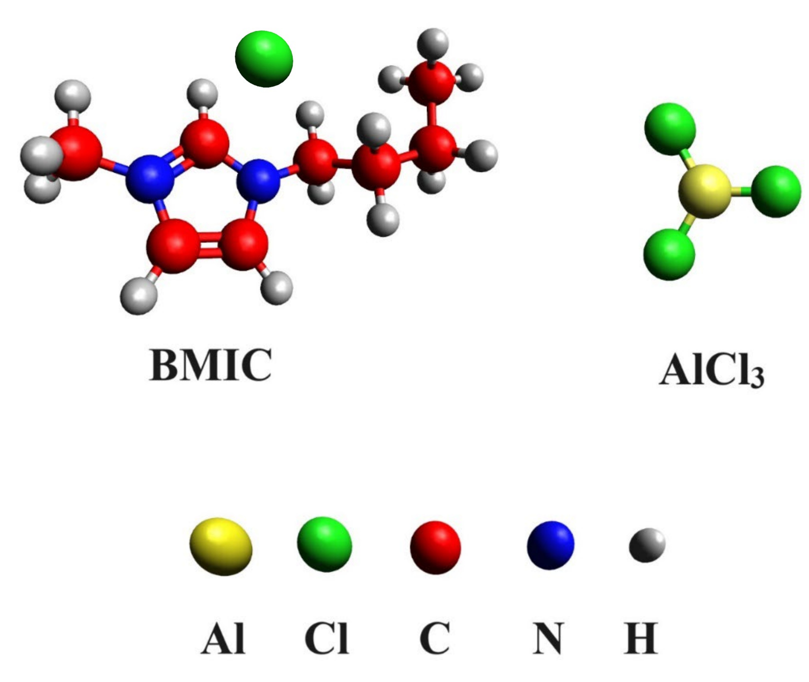


Figure 1 – Molecular structures of BMIC and $AlCl_3$

2 METHODS

In the $AlCl_3$:BMIC IL, the chloroaluminate species attain equilibrium as shown by the following reactions.

$$BMIC = BMI^+ + Cl^-$$

$$AlCl_3 = 0.5Al_2Cl_6$$

$$BMI^+ + AlCl_4^- = BMI^+ + Cl^- + 0.5Al_2Cl_6, \quad K_1 = \frac{a_{Cl^-}\sqrt{a_{Al_2Cl_6}}}{a_{AlCl_4^-}} \quad (1)$$

$$BMI^+ + Al_2Cl_7^- = BMI^+ + AlCl_4^- + 0.5Al_2Cl_6, \quad K_2 = \frac{a_{AlCl_4^-}\sqrt{a_{Al_2Cl_6}}}{a_{Al_2Cl_7^-}} \quad (2)$$

$$BMI^+ + Al_3Cl_{10}^- = BMI^+ + Al_2Cl_7^- + 0.5Al_2Cl_6, \quad K_3 = \frac{a_{Al_2Cl_7^-}\sqrt{a_{Al_2Cl_6}}}{a_{Al_3Cl_{10}^-}} \quad (3)$$

$$BMI^+ + Al_4Cl_{13}^- = BMI^+ + Al_3Cl_{10}^- + 0.5Al_2Cl_6, \quad K_4 = \frac{a_{Al_3Cl_{10}^-}\sqrt{a_{Al_2Cl_6}}}{a_{Al_4Cl_{13}^-}} \quad (4)$$

a_{Cl^-}, $a_{AlCl_4^-}$, $a_{Al_2Cl_7^-}$, $a_{Al_3Cl_{10}^-}$, $a_{Al_4Cl_{13}^-}$, and $a_{Al_2Cl_6}$ are the activity of Cl^-, $AlCl_4^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, $Al_4Cl_{13}^-$ and Al_2Cl_6 respectively.

In this model, neutral Al_2Cl_6 was considered as an anion. X_i is defined as Temkin mole fraction. Summation of the mole fraction of all species is unity [1].

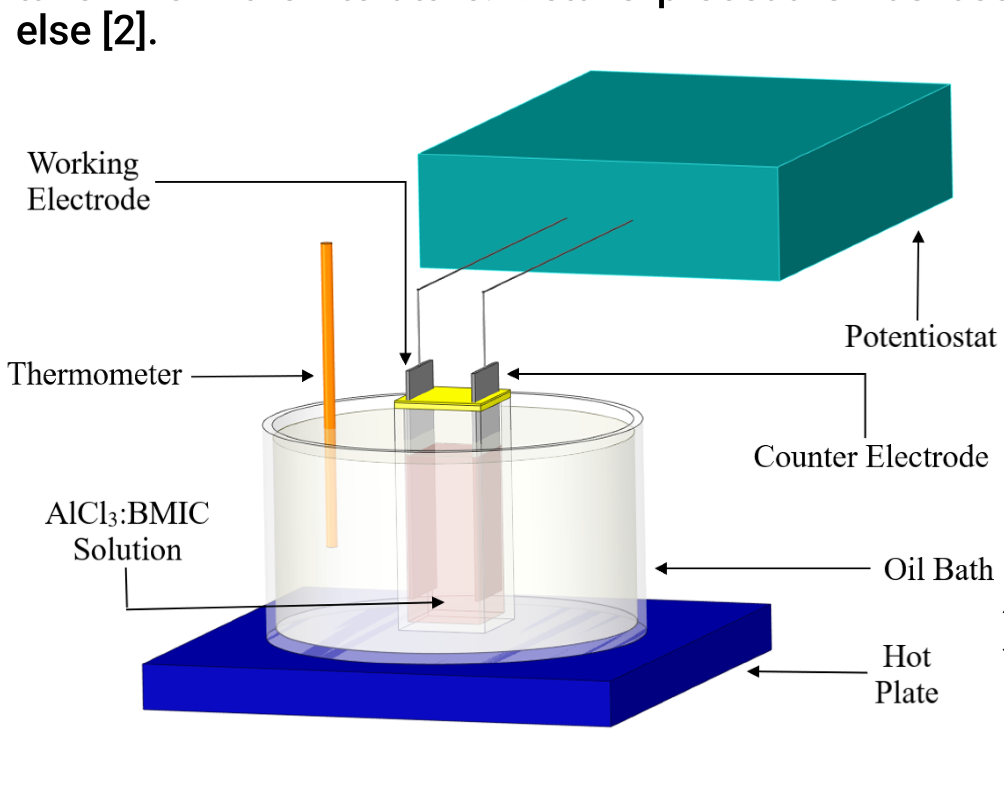
$$X_{Cl^-} + X_{AlCl_4^-} + X_{Al_2Cl_7^-} + X_{Al_3Cl_{10}^-} + X_{Al_4Cl_{13}^-} + X_{Al_2Cl_6} = 1 \quad (5)$$

Based on mass and charge balance, the following equation was established [1].

$$X_{AlCl_4^-} + 2X_{Al_2Cl_7^-} + 3X_{Al_3Cl_{10}^-} + 4X_{Al_4Cl_{13}^-} + X_{Al_2Cl_6}\frac{2-X_{AlCl_3}}{1-X_{AlCl_3}} = \frac{X_{AlCl_3}}{1-X_{AlCl_3}} \quad (6)$$

Activity of the species (a_i) can be expressed as, $a_i = \gamma_i X_i$ where γ_i is activity coefficient. Considering γ_i=1 except for Al_2Cl_6, equations (1) to (6) were solved for X_{AlCl_3} = 0 to 1. γ_i=3 for Al_2Cl_6 [1].

Equilibrium constant value at 25°C for different reactions (K_1, K_2, K_3, and K_4) was taken from the literature. Details procedure has been described in somewhere else [2].



R_2= total resistance of the electrochemical cell (summation of the resistance of leads, electrodes, and electrolyte)

R_1= Charge transfer resistance

W= Warburg impedance

When, electrolyte resistance >> electrode+ leads resistance

R_2 ≈ electrolyte resistance

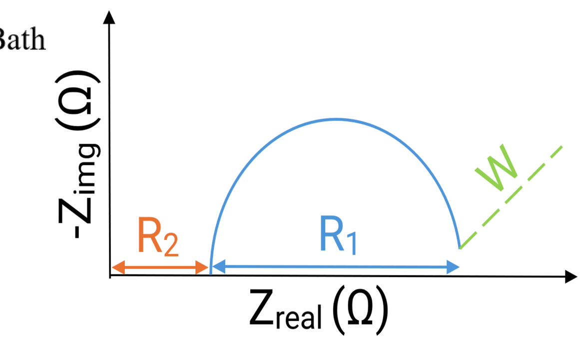
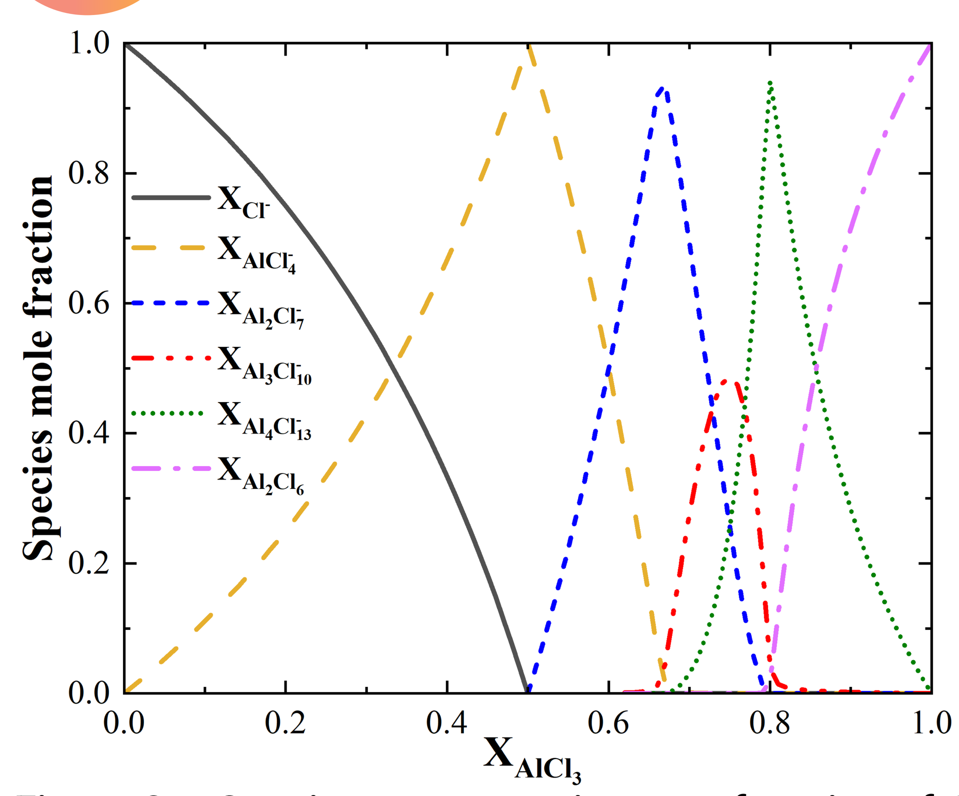


Figure 2 – (left) Illustration of the electrical conductivity measurement setup [2], (right) Nyquist plot

Electrolyte resistance, $R_2 = \rho\frac{d}{H \times W}$; d= distance between the electrodes, H (Height) × W (Width)= area of the electrode, ρ = resistivity of electrolyte; Conductivity of the electrolyte, $\sigma = \frac{1}{\rho}$

3 RESULTS & DISCUSSION



- When X_{AlCl_3} = 0 to 0.50 , only anions are Cl^- and $AlCl_4^-$. Higher order anionic species like $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, and $Al_4Cl_{13}^-$ form above X_{AlCl_3} = 0.50.
- $AlCl_4^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, and $Al_4Cl_{13}^-$ anions reaches high concentration at 0.50, 0.67, 0.75, and 0.80 X_{AlCl_3}, respectively.
- Species distribution does not change much with temperature for chloroaluminate ILs [3].

Figure 3 – Species concentration as a function of $AlCl_3$ mole fraction in $AlCl_3$:BMIC IL at 25°C [2]

- $AlCl_4^-$ has weaker interaction force with BMI^+ cation compared to interaction force between Cl^- and BMI^+. So, $AlCl_4^-$ is more conductive than Cl^-.
- $AlCl_4^-$ has stronger interaction force with BMI^+ cation, relative to the interaction force between $Al_2Cl_7^-$ and BMI^+.
- However, $AlCl_4^-$ has higher conductivity due its higher symmetry and lower size compared to $Al_2Cl_7^-$.
- That is why, $AlCl_4^-$ controls the electrical conductivity of the electrolyte.

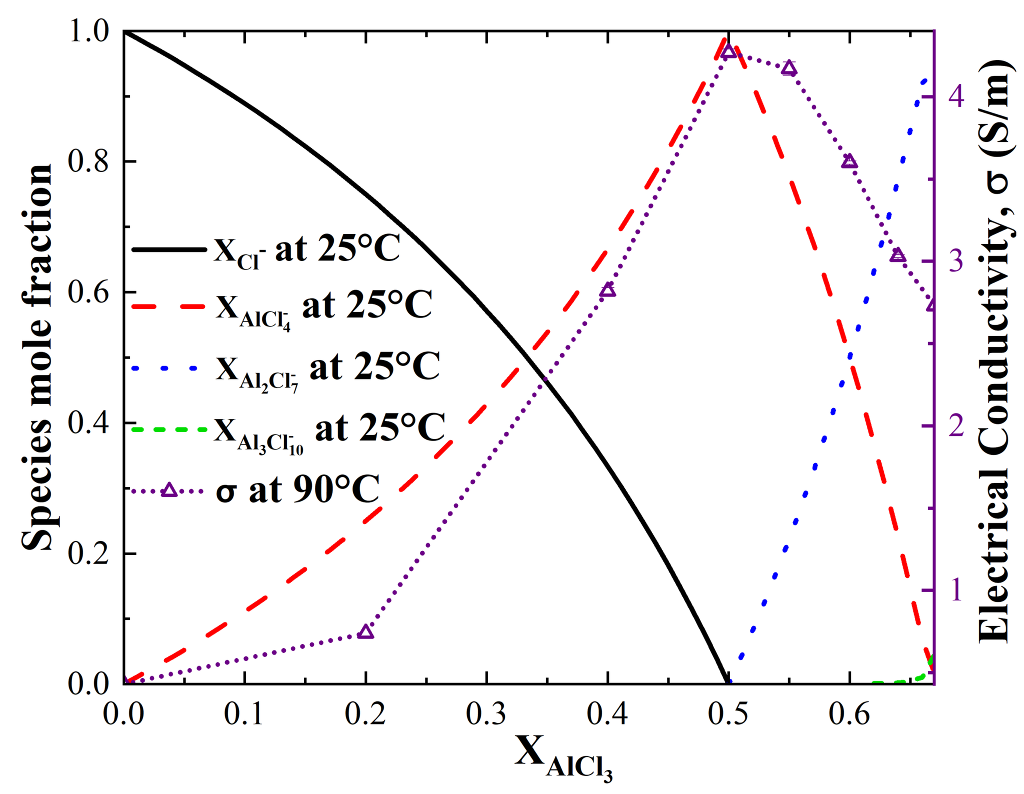
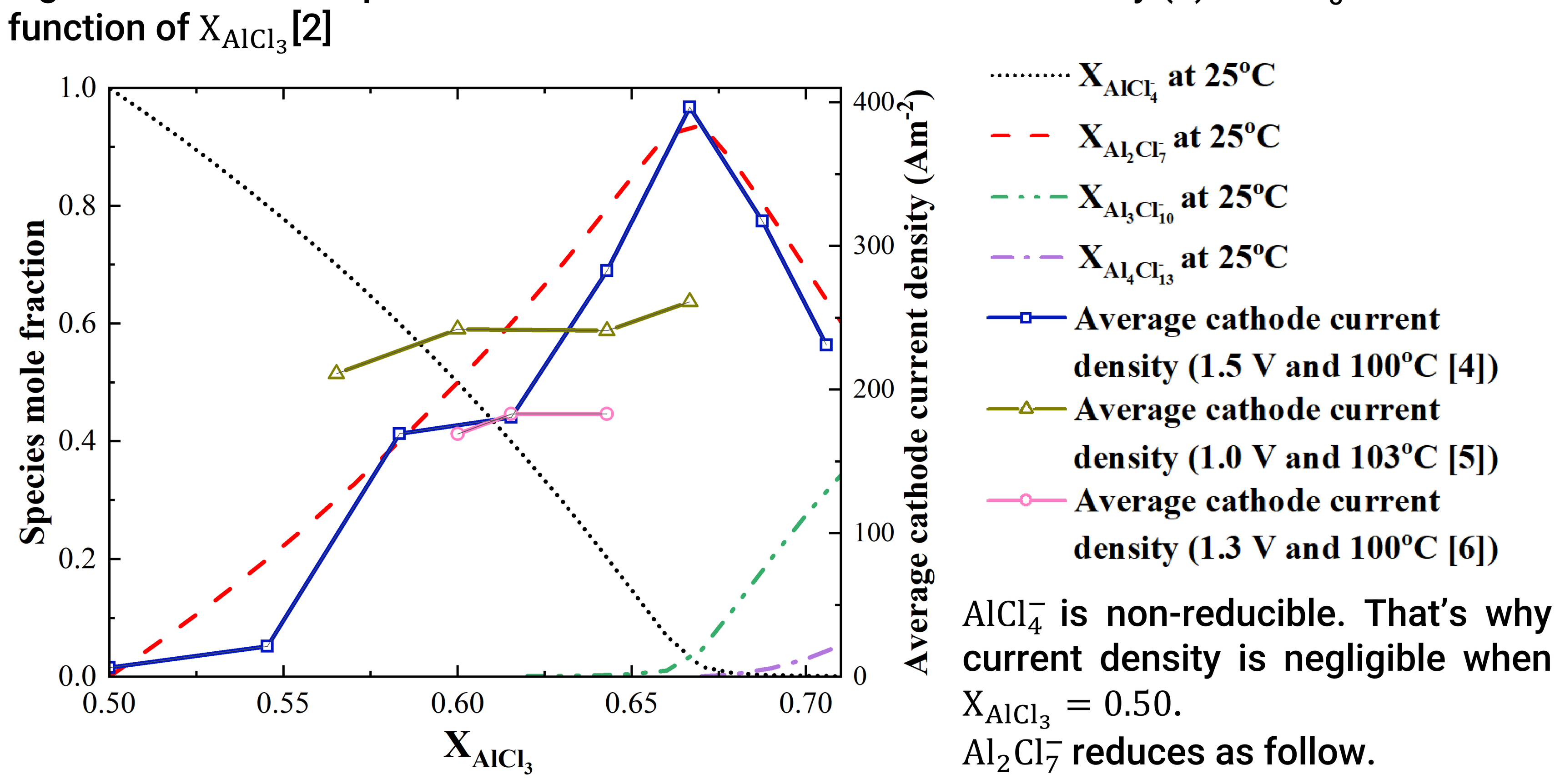


Figure 4 – Different species mole fraction and electrical conductivity (σ) of $AlCl_3$:BMIC as a function of X_{AlCl_3} [2]



$AlCl_4^-$ is non-reducible. That's why current density is negligible when X_{AlCl_3} = 0.50.

$Al_2Cl_7^-$ reduces as follow.

$$4Al_2Cl_7^- + 3e^- = Al + 7AlCl_4^-$$

Figure 5 – Species mole fraction ($X_{AlCl_4^-}$, $X_{Al_2Cl_7^-}$, $X_{Al_3Cl_{10}^-}$, and $X_{Al_4Cl_{13}^-}$) at 25°C and average cathode current density for Al electrodeposition in $AlCl_3$:BMIC [4-6]

4 CONCLUSIONS

- A thermodynamic model of $AlCl_3$:BMIC was constructed incorporating species Cl^-, $AlCl_4^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, $Al_4Cl_{13}^-$, and Al_2Cl_6.
- Electrical conductivity of $AlCl_3$:BMIC depends on $AlCl_4^-$ because of its weaker interaction with BMI^+ compared to interaction force between Cl^- and BMI^+, and higher symmetry and lower size relative to $Al_2Cl_7^-$.
- The average current density at the cathode during aluminum deposition is mainly controlled by the reducible $Al_2Cl_7^-$ anion.

REFERENCES

1. H. Øye, M. Jagtoyen, T. Oksefjell and J. Wilkes, In Materials Science Forum, (Trans Tech Publ: 1991), pp 183-190.
2. M.K. Nahian and R.G. Reddy, Journal of Physical Organic Chemistry, 36, e4549 (2023).
3. A.N. Ahmed, M.K. Nahian and R.G. Reddy, Metallurgical and Materials Transactions B, 1-8 (2024).
4. Y. Wang, (The University of Alabama: 2020).
5. V. Kamavaram, D. Mantha and R. Reddy, Electrochimica acta, 50, 3286-3295 (2005).
6. V. Kamavaram, D. Mantha and R. Reddy, *Journal of Mining and Metallurgy B: Metallurgy*, 39, 43-58 (2003).