**Supporting Information**

**Effect of electrolyte additive on** **the** **electrochemical** **stability of aluminum-graphite battery**

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To select the appropriate additives to improve the electrochemical performance of aluminum batteries, we studied the effects of several additives on the viscosity, conductivity, and anodic limit potential of acetamide-AlCl3 in detail. The additives included two categories: (1) alkali metal halides (LiCl, LiBr, NaCl, NaBr), which were often chosen because of their relatively small ion radius; (2) organics: ethylene carbonate (EC), tetrahydrofuran (THF), 1,2-dichloroethane (DCE), which were often used as solvents in the lithium-ion battery because of large dielectric constant and low viscosity. The results were shown in table S1.

As shown in table S1, the viscosity of acetamide-AlCl3 tends to increase by alkali metal halides. The viscosity of acetamide-AlCl3 with DCE/THF is lower than that of the acetamide-AlCl3 system. The positive impact of DCE was most significant. The electrical conductivities increase by almost all additives except EC for acetamide-AlCl3. The anodic limit potential (*E*lim) is an important factor for acetamide-AlCl3 used as the electrolyte of aluminum-ion batteries. The *E*lim removes to a negative potential of near 1.90 V with the addition of LiBr and NaBr. Other additives increase the *E*lim, and it is obvious in acetamide-AlCl3-LiCl/NaCl/DCE that the anodic limit potential increases to about 2.45 V from 2.37 V.

**Table S1** Viscosity (*η*), electrical conductivity (*σ*), and anodic limit potential (*E*lim) of acetamide-AlCl3 (molar ratio = 1.3) with/without various additives (5 mol%) at 313K

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | Blank | LiCl | LiBr | NaCl | NaBr | EC | THF | DCE |
| *η*/(mP·s) | 46.144 | 45.960 | 46.537 | 44.799 | 47.528 | 46.478 | 41.364 | 40.904 |
| *σ*/(mS·s-1) | 2.35 | 2.70 | 2.58 | 2.52 | 2.50 | 2.19 | 2.46 | 2.45 |
| *E*lim/V | 2.37 | 2.44 | 1.93 | 2.45 | 1.95 | 2.37 | 2.37 | 2.45 |



**Figure S1.** SEM images of the Al deposits in acetamide-AlCl3 (r = 1.3) at room temperature: (a) blank; (b) LiCl; (c) LiBr; (d) NaCl; (e) NaBr; (f) EC; (g) THF; (h) DCE

The effect of electrolyte additives on the morphologies of aluminum deposit on the aluminum substrate was also studied in acetamide-AlCl3 (r = 1.3). The deposits are greatly improved by adding additives except NaBr as shown in Fig. S1. The compact and flat aluminum deposit covers the entire substrate. Fine deposits but with cracks are obtained by the addition of LiCl/LiBr. Granular deposits are obtained by the addition of NaCl/EC/THF. The deposit consisted of a columnar structure is obtained from AlCl3-acetamide-DCE system. Thus, deposits become compact and flat by NaCl, EC, THF, and DCE in acetamide-AlCl3.

Previous studies had shown that additives DCE and EC can effectively improve the deposition/dissolution efficiency of aluminum in AlCl3-based electrolytes for Al-graphite battery.1 Canever reported that dichloromethane (DCM) seemed to perform best by having excellent miscibility with the electrolyte and no apparent reactivity. Additive DCM in AlCl3-based electrolyteincreased the specific capacity without sacrificing its coulombic efficiency.2

The physicochemical properties parameters of 1,2-dichloroethane (DCE) and dichloromethane (DCM) are listed in table S2. Additive DCE is more consistent with electrolyte requirements: wide temperature adaptability, low density, and high conductivity.

**Table S2** Physicochemical properties of 1,2-dichloroethane (DCE) and dichloromethane (DCM)

|  |  |  |  |
| --- | --- | --- | --- |
|  | Boiling point/℃ | Dielectric constant/(C²/(N·M²)) | Density/(g cm-3) |
| DCE | 83.5 | 10.4 | 1.256 |
| DCM | 39.8 | 8.93 | 1.325 |

Based on the above observation, additives DCE improves the physicochemical properties of the AlCl3-acetamide electrolyte. Meanwhile, it also improves the Al deposit morphology and deposition/dissolution efficiency on the Al anode. Therefore, DCE is considered to further study its effect on the electrochemical performance of Al-graphite-type batteries in this paper.

# References

1. J. H. Yue, L. Z. Gao, X. P. Yue, and Y. G. Zhao, *Energy Energy Conser.*, **2**, 68 (2011).
2. N. Canever, N. Bertrand, and T. Nann, *Chem. Commun.*, **54**, 11725 (2018).