

Electronic Supplementary Information (ESI)

A joint experimental and theoretical determination of the structure of discharge products in Na–SO₂ battery

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Procedure for a storage test of pristine electrolyte ($\text{NaAlCl}_4 \cdot x\text{SO}_2$)

The electrolyte ($\text{NaAlCl}_4 \cdot x\text{SO}_2$) was prepared by thoroughly mixing sodium chloride (NaCl , >99.9%, Alfa Aesar) with aluminum chloride (AlCl_3 , 99.999%, Alfa Aesar) at a ratio of 1.1 to 1.0 in a homemade glass/Teflon vessel. The vessel was then flushed with SO_2 gas (Fluka) for two hours until the solid mixtures were fully converted into transparent liquids. In detail, 20.0 g of AlCl_3 (150.0 mol) and 8.77 g of NaCl (150.0 mol) were finely dispersed in the vessel and thereafter excess amounts of SO_2 gas were blown into the vessel controlled with pressure of 1.5 atm for two hours. After the electrolyte preparation was completed, we calculated the mass of SO_2 that participated in the formation of the electrolyte complex by weighing the vessel reactor, as shown in the following equation.

$$\text{Used } \text{SO}_2 \text{ mass for electrolyte preparation} = \text{Mass of vessel after reaction } (\text{AlCl}_3 + \text{NaCl} + \text{vessel} + \text{SO}_2) - \text{mass of vessel before reaction } (\text{AlCl}_3 + \text{NaCl} + \text{vessel})$$

It should be noted that there is unreacted gaseous SO_2 in the vessel even after the reaction was completed because excess amounts of SO_2 were used for this reaction. Therefore, we bent the electrolyte vessel each day in order to remove unreacted SO_2 remaining in the vessel and carefully monitored the change of vessel mass. After this repeated process for nine days, we observed that 2.20 mol of SO_2 was attached on the NaAlCl_4 complex.

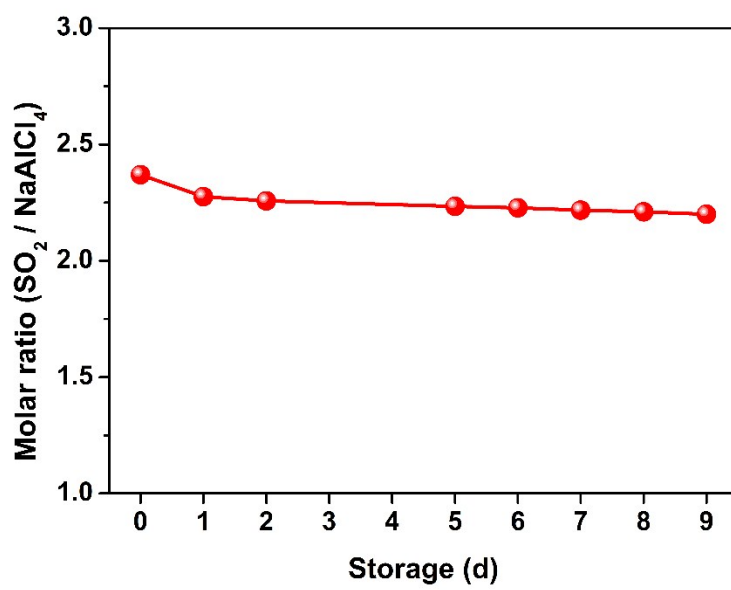


Figure S1. Storage tests for pristine electrolyte to determine coordination number of SO₂.

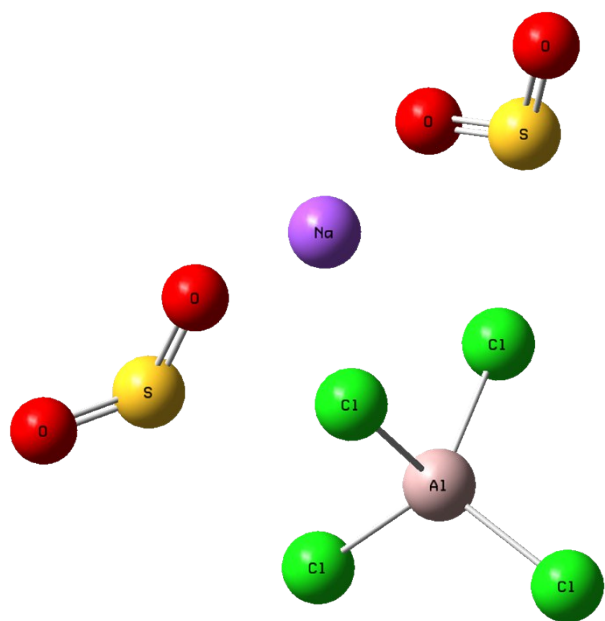


Figure S2. Optimized chemical structure of NaAlCl₄•2SO₂.