Mechanism of Reaction in NaAlCl₄ Molten Salt Batteries with Nickel Felt Cathodes and Aluminum Anodes. Part II: Experimental Results and Comparison with Model Calculations.

The battery systems: Al/NaCl-AlCl₃-Al(2)X(3)/Ni-felt (X = S, Se, Te) and the corresponding system without chalcogen have been studied experimentally at 175 degrees C. Charge/discharge experimental performed on cells with NaCl saturated melts, show that advantages with regard to rate capability and cyclability can be obtained with systems containing dissolved chalcogen compared with the chalcogen-free system. Exchange of chalcogen between cathode and electrolyte during cycling was confirmed by performing gravimetric analysis and Raman spectroscopy of the electrolytes. Cathode reactions were studied by coulometric titrations (performed on cells with slightly acidic NaCl-AlCl₃ melts and small amounts of chalcogen) and compared with model calculations. Cells containing chalcogen revealed at least three voltage plateaus during cycling. The lowest plateau is associated with formation/decomposition of essentially Ni₄S₉z and Ni₄Se₉z in the sulfide and selenide system, respectively. Cells containing selenide revealed extra capacity below the Ni₄Se₉z-plateau, most probably associated with a Al₄Ni₄S₉z compound. On the second plateau of sulfide systems NiCl₂ or a Ni₄S₉Cl₂y-2z compound with y > (4.4 +/- 0.2), z is formed during charging. Reduction of the formed compound to Ni takes place via consumption of sodium chloride. For acidic melts, sulfide at the cathode was found to be present as...