Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Using Molten Salts to Probe Outer-Coordination Sphere Effects on Lanthanide(III)/(II) Electron-Transfer Reactions

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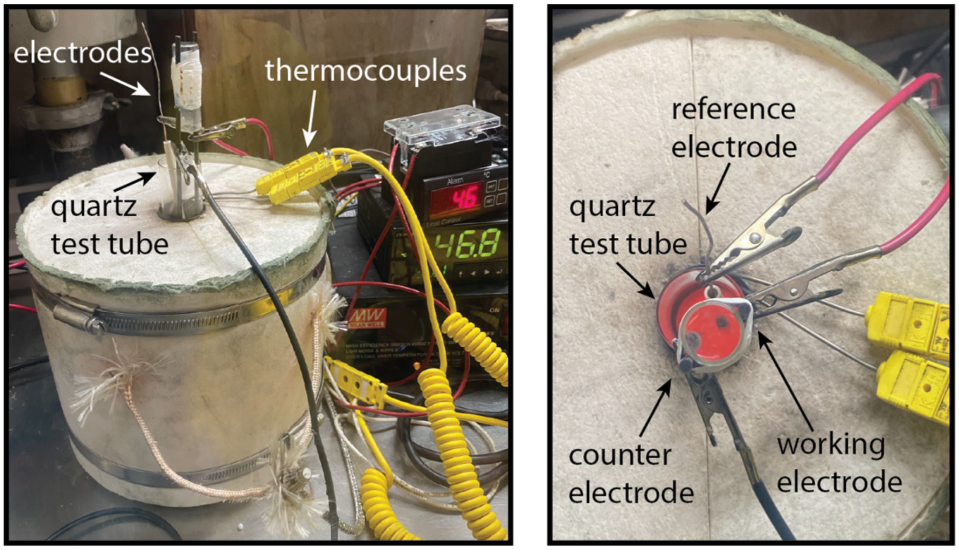


Figure S1. Photographs of the furnace used for electrochemical measurements in molten salts. Side view with electrodes extending out of the hole in the center of the furnace (*left*). Top view showing arrangement of the electrodes within the furnace (*right*). The furnace (6 in. tall) was composed of alumina based ceramic fiber insulation (3-1/8 in. thickness) that covered two 180° semi-cylindrical ceramic heating elements (2 in. tall, 1.25 in. inner diameter, 100 W, 28.5 V). These heating elements were arranged around a central hole (diameter 1.25 in.; Figure S1). The hole was bored through the top of the apparatus ending approximately 2 in. above the bottom of the insulation. A steel tube (outer diameter = 3.1 cm, length = 10 cm) was inserted into this hole to act as a liner within the furnace and hold an electrochemical cell in place in the center of the heating elements. The electrochemical cell was a quartz test tube (2.7 cm outer diameter, 13.5 cm tall, 0.1 cm wall thickness). The outer walls of the furnace were wrapped in a fiber blanket insulation layer (about 5 mm thick).

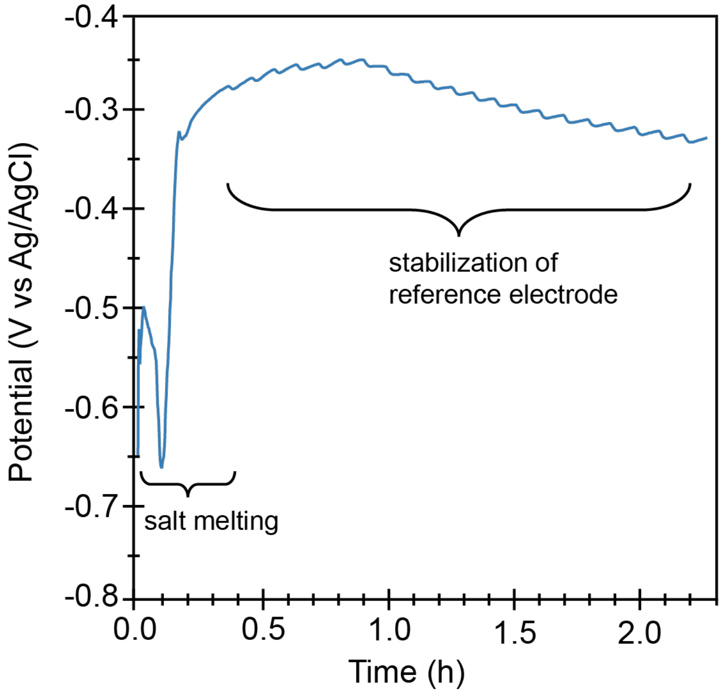


Figure S2. Open circuit potential variation over time demonstrating the stabilization of a Ag/AgCl (molten KCl) reference electrode at 850 °C. The initial jump in potential occurred as the salt melted and reached 850 °C. The gradual change in potential after about 0.5 hours occurred as salt ions permeated the mullite membrane. The reference electrode was stabilized after about 2 hours of heating. The step shape of the curve after melting was due to small fluctuations in temperature as the furnace controller kept the temperature at 850 ± 5 °C. The working electrode was a glassy carbon rod.

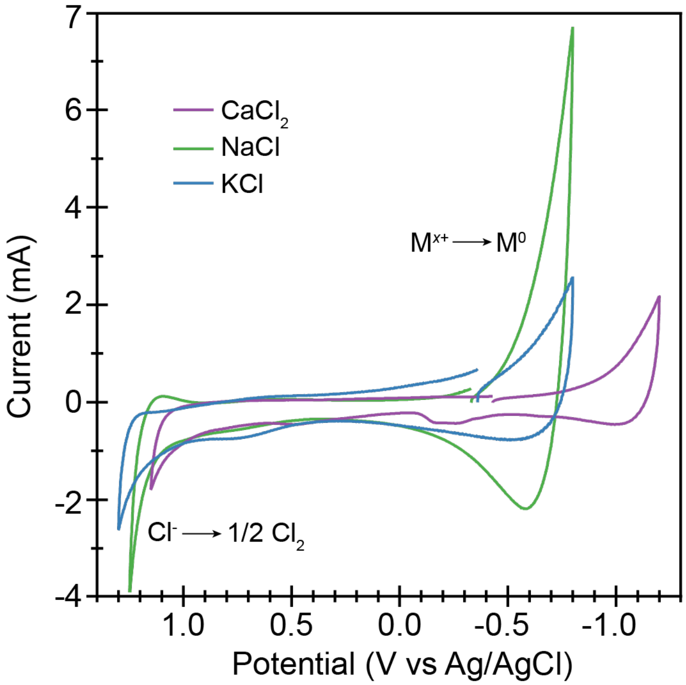


Figure S3. Cyclic voltammograms of molten salts ($CaCl_2$, NaCl, and KCl) at 850 °C. Anodic current onset at around +1.2 V was Cl^-/Cl_2 oxidation, and cathodic current onset at around -0.5 to -1.0 V was M^{x+}/M^0 reduction (M = Ca, Na, K). The working and counter electrodes were glassy carbon rods and the reference electrode was a silver wire immersed in a solution of AgCl (1% wt.) in the corresponding molten salt and was encased in a mullite tube.

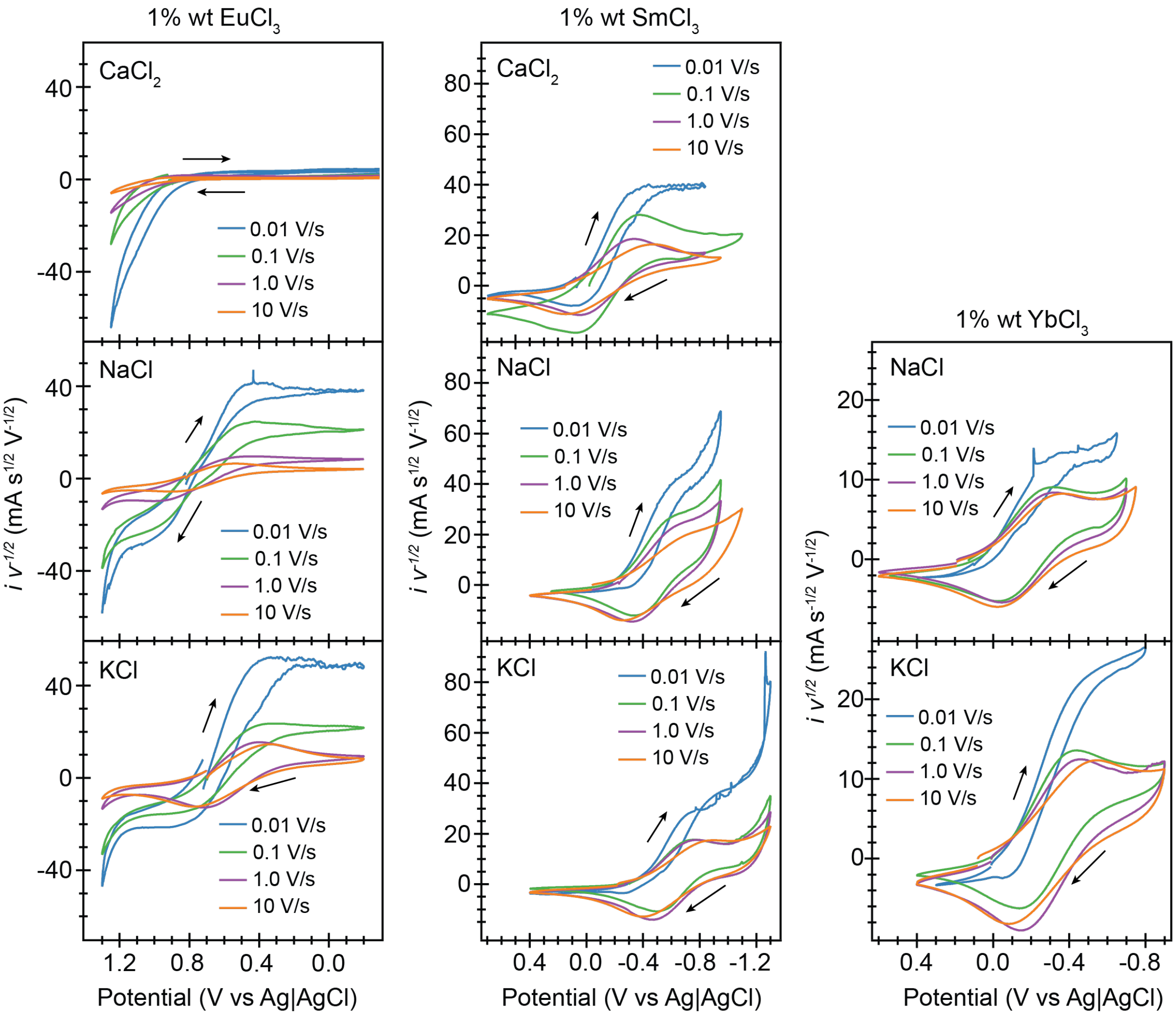
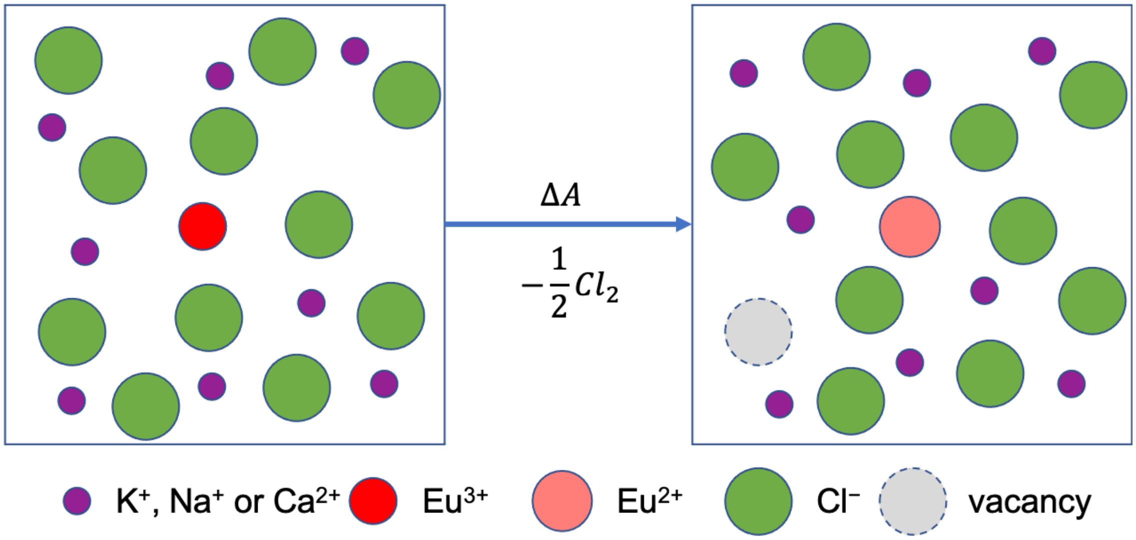


Figure S4. Cyclic voltammetry of $LnCl_3$ (Ln = Eu, *left*; Sm, *middle*; Yb, *right*) at varied scan rates in molten $CaCl_2$ (*top*), NaCl (*middle*), and KCl (*bottom*) at 850 °C. Arrows show the scanning direction. The reference electrode was a silver wire immersed in a solution of AgCl (1% wt.) in the corresponding molten salt and was encased in a mullite tube. Electrochemical measurements in $CaCl_2$ did not include $YbCl_3$ because of Yb insolubility in this matrix. The trend towards sigmoidal shapes at slower scan rates is likely due to convection within the molten salt because of a temperature gradient moving away from the electrode surface.



Scheme S1. Schematic diagram of the thermodynamic process for the calculation of Eu^{3+}/Eu^{2+} reduction. “Vacancy” is used for the reduced state after the release of Cl_2.