SPECTROELECTROCHEMICAL INVESTIGATIONS OF MOLTEN HALIDE SOLUTIONS

Dr Gleb Mamantov

University of Tennessee
Dept of Chemistry
552 Buehler Hall
Knoxville TN 37996-1600

AFOSR/NL
110 Duncan Ave Suite B115
Bolling AFB DC 20332-0001

Capt Hugh De Long

The main objective of this research, performed by Ellen Kurt Hondrogiannis, a graduate student at the University of Tennessee, was to investigate the utility of the combination of spectroscopy and electrochemistry, or spectrotelectrochemistry (SEC), for studies of redox processes in molten halides. Three studies were done in the course of this work.
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Spectroelectrochemical Investigations of Molten Halide Solutions

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Gleb Mamantov
Principal Investigator
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The utilities of two fiber optic probing techniques, fiber optic cables connected to the dry box and a fiber optic probe for in situ studies, have been demonstrated. The Raman, UV-visible, and electron spin resonance (ESR) spectroelectrochemical behavior of chloranil in basic melt (<50 m/o AlCl₃) and the UV-visible and the ESR spectroelectrochemical behavior of chloranil in basic melt (<50 m/o AlCl₃) has been examined. The chloranil is electrochemically reduced in the basic melt via two one electron transfers. The results indicate that the radical anion intermediate exists as a complex with AlCl₃ (or Al₂Cl₇) in both basic and acidic melts.

UV-visible spectroscopic and spectroelectrochemical studies of NbCl₅ in the basic melt showed that a Nb²⁺⁺ cluster is electrochemically generated in the fourth reduction and that it is further generated chemically by the disproportionation reaction of Nb⁴⁺, produced in the first wave, to Nb⁵⁺ and Nb³⁺, the latter of which then decomposes to give the cluster. The cluster was shown to be less soluble at higher temperatures.

The UV-visible spectroscopic and spectroelectrochemical behavior of potassium hexachlororhenenate (IV) was studied. The initial voltammograms show a new wave to grow in at a potential more positive than the [ReCl₆]²⁻ reduction. The resulting voltammogram, consisting of three reduction and two oxidation waves, does not change further. Spectroelectrochemical results indicate that this first reduction is due to the [Re₂Cl₆]²⁻/[ReCl₃]²⁻ couple. The second wave is believed to be due to the reductions of both [ReCl₆]²⁻ and [Re₂Cl₆]²⁻. The results are complicated by the instability of rhenium (III).

A list of publications resulting from this work is attached.
PUBLICATION LIST:


