

Study of Counter Ion Mass Transport in Ruthenium
Complex Melts

Wei Wang, Dongil Lee and Royce W. Murray*

Kenan Laboratories of Chemistry, University of North
Carolina, Chapel Hill, North Carolina 27599-3290

Abstract

Recent work on redox polymer molten salts shows that the apparent electron transfer rate in molecular melts can be determined by the physical diffusion of electro-inactive counter ions. The physical diffusion rates of electro-inactive perchlorate and electro-active iodide counter ions in ruthenium bipyridine complex melts has been measured by two different methods: alternative current (AC) impedance measurement and potential step chronoamperometry. The chronoamperometric measurement were done in ruthenium complex melts, $[\text{Ru}(\text{bpy}(\text{CO}_2\text{MePEG}_{350})_2)_3][\text{X}]_2$, containing mixed perchlorate and iodide counter ions, where the iodide was the minor population. Cyclic voltammograms in either dilute solution or undiluted melts show two well resolved oxidation peaks of iodide and a single wave of ruthenium (II/III). The AC impedance measurement was done on melts containing only perchlorate counter ions. The mass transport data for counter ions from these two different methods were in good agreement with each other. The ion atmosphere control of electron transfer in the ruthenium complex melt is supported by the linear relation of electron transfer rate constant for ruthenium (II/III) reaction and physical diffusion coefficient of perchlorate in a logarithmic plot with unity slope.

Acknowledgement to Department of Energy for support of this research.