

**Counterion Atmosphere Relaxation and
Electrochemical Dynamics in Semisolid Films on
Electrodes**

Royce W. Murray

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

Recent results[1,2] on the behavior of electrodes coated with films of electroactive, semi-solid, undiluted molecular melts implicate the importance of counterion diffusivity in the dynamics of both heterogeneous and homogeneous electron transfers in such melts. The molecular melts are Co poly-pyridine complexes with short polyethylene glycol chains attached to either the ligand or the counterion of the metal complex.

Our laboratory has previously reported that rates of electron transfers in semisolids are slower and offer larger energy barriers than analogous reactions in fluid solutions. Hypotheses for the origins of these differences have included inner sphere barrier effects and solvent dynamics. The "solvent" is a polyether shell around each electroactive entity. New evidence, including the use of plasticization of charge transport parameters in a redox film by partition of CO₂ from liquid CO₂ bathing the film, favors a form of solvent dynamics lodged in rate-controlling, coulombically motivated relocation of counterions following or accompanying rapid electron transfer. This evidence and results from continuing studies will be presented.

Supported by NSF, DOE, NSF S&T Center at
UNC

[1] Lee, D.; Hutchison, J. C.; Leone, A. M.; DeSimone, J. M.; Murray, R. W., *J. Amer. Chem. Soc.*, **2002**; *124*, 9310-9317.

[2] Lee, D.; Harper, A. S.; DeSimone, J. M.; Murray, R. W., submitted.