Development and Application of Novel Iterative Electroanalytical Approaches to Characterization of Bulk Redox Conducting Systems

Pawel J. Kulesza[1] and Adam Lewera[1]

[1]university of Warsaw
Department of Chemistry
Pasteura 1
Warsaw, PL 02-093
Poland

We propose and describe novel absolute electroanalytical approaches that allow determination of both the concentration of redox sites and the apparent diffusion coefficient for charge propagation in bulk redox conducting solids, semisolids and solutions. A Keggin-type single crystal of dodecatungsto-phosphoric acid will be used as a model bulk inorganic material for solid-state voltammetry, and it can be readily investigated using an ultramicrodisk working electrode in the absence of external liquid supporting electrolyte. The proposed method requires numerical solution of the combination of two equations, namely of the first one describing current (or charge) in a well defined (either spherical or linear) diffusional regime with the second general equation describing amperometric or Normal Pulse Voltammetric current under mixed (linear ? spherical) conditions. The iterative approach is based on successive approximations through calculation and minimizing of the least square error function. The method is fairly universal and, in principle, it can be extended to the investigation of other bulk systems including sol-gel processed materials, redox melts and solutions on condition that they are electroactive and well behaved, they contain redox centers at sufficiently high level, and the number of electrons for the redox reaction considered is known. Special attention is paid to the importance of diagnostic experiments.