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Determining thermodynamic properties of Ba and Sr in liquid bismuth using EMF technique

Hojong Kim, Nathan Smith and **Timothy Lichtenstein**
Pennsylvania State University, USA

The thermodynamic properties of Ba-Bi and Sr-Bi alloys were determined by electromotive force (EMF) measurements to evaluate the viability of liquid bismuth metal as a medium for separating alkaline-earth species from molten salt electrolyte. EMF values of various Ba-Bi and Sr-Bi alloy compositions were measured at ambient pressure as a fuction of temperature between 700 K and 1050 K at mole fractions xBa or xSr=0.05-0.80. Binary solid-state electrolytes (CaF_2-BaF_2 or CaF_2-SrF_2) were employed to fabricate two types of electrochemical EMF cells: Ba(s)|CaF_2-BaF_2|Ba-Bi and Sr(s)|CaF_2-SrF_2|Sr-Bi. Reproducible EMF values within ±5 mV were obtained during cooling-heating cycle at dilute alloy compositions (xBa or Sr<0.35), as shown in Figure 1a; increased thermal hystesis was apparent for higher alloy compositions (xBa or Sr>0.35) due to the formation of meta-stable phases. For each alloy composition, reported are the measured activity, the excess partial molar Gibbs energy, and temperature-independent partial molar entropy and enthalpy of alkaline-earths (Ba and Sr) in Bi, as well as the phase transition temperatures. Combining the high liquid-state solubility of Ba and Sr in Bi and the strong chemical interactions with Bi metal (e.g., aSr as low as 1.2 10–13), Bi shows promise as an electrode material for separating alkaline-earth species from molten salt electrolytes (e.g., LiCl-KCl-$SrCl_2$). The EMF measurements were further corroborated using power X-ray diffraction (XRD) and differential scanning calorimetry (DSC) to determine the relevant crystal structures and phase transition temperatures for each alloy composition. These data were used to construct revised binary phase diagrams over a wide range of composition range.

huk29@psu.edu

Electroanalytical methods in characterization of sulfur and organic matter species in water environment

Irena Ciglenečki, Marija Marguš and **Ivana Coha**
Ruđer Bošković Institute, Croatia

Electroanalytical methods due to its simplicity and prompt response, low cost and relatively high sensitivity and selectivity, are shown to be good alternative analytical techniques for characterization and quantification of different sulfur and organic matter species including nanoparticles (NPs) in water environment. In the frame of the project "The sulphur and carbon dynamics in the sea- and fresh-water environment" (SPHERE), funded by Croatian science foundation we are studying sulphur (S) and carbon (C) dynamics between different environmental compartments (atmosphere, water, sediment, biota) of the sea- and fresh-water environment. A main focus is on the distribution between organic, inorganic, dissolved, colloidal and nano-particulate fraction. Voltammetric measurements in combination with electrochemical nanogravimetric measurements (EQCM) and atomic force and scanning tunneling microscopy (AFM, STM) on different electrode surfaces (Hg,Au) are shown to be beneficial in giving more details and information related to attachment, adsorption, deposition and interaction between selected sulfur species, including NPs and functionalized electrode surfaces. Several experiments were designed to monitor in parallel to voltammetric and amperometric measurements, physicochemical and surface characteristics (ζ – potential and size) of the studied metal sulfide NPs (FeS, PbS, Ag2S and CdS) under same experimental conditions. It was shown that electrochemical signals produced by studied NPs from bulk solution and measured by DLS, ζ - potential and size of the same NPs, is changing with electrolyte concentrations as well as with its composition. The measurements indicate significant relationship between measured ζ – potential and size of the studied metal sulfide NPs dispersions and recorded voltammetric and amperometric peak charges, indicating great potential of electroanalytical chemistry in characterization of physico-chemical and surface chemistry features of the metal sulphide NPs in the water environment. The best electrochemical response is obtained in presence of the smaller NPs, <100 nm. Methodology that was developed in laboratory, in model water conditions was further applied for the study of natural sea- and freshwater samples including aerosols and rain precipitation.

irena@irb.hr