

Solid State Electrochemical Approaches to Characterization of the Thermodynamic Stability of Ternary Alkali Metal Compounds

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The characterization of the thermodynamic stability of most of the alkali metal-containing ternary compounds, i.e. A-Me-O (A = Li, Na, K; Me = Al, Si, B, P, Nb, Mo, Ti, Zr, Hf etc.), is complicated due to the extremely low level of the alkali activity to be measured. Therefore, thermodynamic data resulting from conventional electrochemical measurements may be distorted by electronic transference through the alkali ion conducting solid electrolyte used in such measurements. In order to overcome this problem, new experimental approaches have been put forward that are based on potentiometric solid electrolyte galvanic cells with yttria stabilized zirconia as the solid electrolyte. The cells, though being oxygen concentration chains, enable alkali and alkali oxide activity, respectively, to be determined by a conversion of the alkali chemical potential into the oxygen potential. As a particular advantage, two of the approaches allow *in situ* checks of the establishment and maintenance of the phase equilibria upon changing the proportions of the phases to be characterized. That way, univariant equilibria can be distinguished from equilibria comprising compounds with a homogeneity region, the evidence of non-stoichiometry being by far more sensitive than by X-ray diffraction. The use of the measuring techniques is substantiated by a number of examples that give partial insight into new aspects of the thermodynamics of the respective compounds.