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Thermoelectric Powers of Cells With NaF–AlF_3–Al_2O_3 Melts

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Abstract

A thermodynamic description of the Peltier heat at the aluminum and the oxygen electrode in the system NaF–AlF_3–Al_2O_3 is given. The thermoelectric power in melts with molar ratios n_{NaF}/n_{AlF_3} from 3.0 to 1.0, saturated with alumina are measured. Seebeck coefficients for molten fluoride electrolytes saturated with alumina, electrolytes that are relevant for aluminum electrowinning electrolysis cells, are reported. The results allow determinations of Peltier heats of aluminum, oxygen and carbon electrodes in NaF–AlF_3 electrolytes saturated with alumina. For molar ratios of n_{NaF}/n_{AlF_3} between 2.6 and 1.2, there is a Peltier heating of the aluminum cathode. This heating is in the same order of magnitude as the electrolyte Joule heat, when the current density is 0.7 A cm^{-2}. For molar ratio n_{NaF}/n_{AlF_3} equal to 1.0 the Peltier effect at the aluminum electrode approaches zero. From theoretical considerations we expect a drop also for molar ratio 3.0. For the anode we report a Peltier cooling that is larger than the heat produced by the anodic overvoltage, in melts with NaF/AlF_3 molar ratio between 2.6 and 1.2 saturated with alumina.

1. Introduction

It is important to control the energy flow and temperature variations in electrochemical reactors. Irreversible heat effects related to the electric current flow may lead to local cooling or heating. Freezing of the electrolyte has been observed in molten salt electrolysis cells, followed by an increase in the cell voltage [1]. Overheating may lead to a breakdown of the cell, or electrolyte boiling. The operating temperature in such cells depends not only on the ohmic resistance, but also on the magnitude of the irreversible heat effect at the electrodes, or in other words, the Peltier heat of the

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