Roles of Cationic and Elemental Calcium in the Electro-Reduction of Solid Metal Oxides in Molten Calcium Chloride

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Previous work, mainly from this research group, is re-visited on electrochemical reduction of solid metal oxides, in the form of compacted powder, in molten CaCl₂, aiming at further understanding of the roles of cationic and elemental calcium. The discussion focuses on six aspects: 1.) debate on two mechanisms proposed in the literature, i. e. electro-metallothermic reduction and electro-reduction (or electro-deoxidation), for the electrolytic removal of oxygen from solid metals or metal oxides in molten CaCl₂; 2.) novel metallic cavity working electrodes for electrochemical investigations of compacted metal oxide powders in high temperature molten salts assisted by a quartz sealed Ag/AgCl reference electrode (650 °C – 950 °C); 3.) influence of elemental calcium on the background current observed during electrolysis of solid metal oxides in molten CaCl₂; 4.) electrochemical insertion/inclusion of cationic calcium into solid metal oxides; 5.) typical features of cyclic voltammetry and chronoamperometry (potentiostatic electrolysis) of metal oxide powders in molten CaCl₂; and 6.) some kinetic considerations on the electrolytic removal of oxygen.

Key words: Electro-Reduction; Calciothermic Reduction; Reactive Metal Oxides; Molten Calcium Chloride; Cyclic Voltammetry; Metallic Cavity Electrode.