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

Guohong Qiu\textsuperscript{a}, Kai Jiang\textsuperscript{a}, Meng Ma\textsuperscript{a}, Dihua Wang\textsuperscript{a}, Xianbo Jin\textsuperscript{a,\textbf{b}}, and George Z. Chen\textsuperscript{a,\textbf{b}}

\textsuperscript{a} College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, 430072, P. R. China
\textsuperscript{b} School of Chemical, Environmental and Mining Engineering, University of Nottingham, Nottingham, NG7 2RD, UK

Reprint requests to G. Z. C.; E-mail: george.chen@nottingham.ac.uk


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 CaCl\textsubscript{2}, 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 CaCl\textsubscript{2}; 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 \degree C–950 \degree C); 3.) influence of elemental calcium on the background current observed during electrolysis of solid metal oxides in molten CaCl\textsubscript{2}; 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 CaCl\textsubscript{2}; and 6.) some kinetic considerations on the electrolytic removal of oxygen.

\textit{Key words:} Electro-Reduction; Calcothermic Reduction; Reactive Metal Oxides; Molten Calcium Chloride; Cyclic Voltammetry; Metallic Cavity Electrode.