Phase Chemistry Study to Support the Technology Development for the Recycling of Lithium Ion Batteries

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The use of the lithium ion batteries has significantly increased over the last few years and is expected to increase in the future, mainly due to their application in electrical cars [1]. Recycling of the batteries is essential to safely dispose hazardous materials as well as to recover valuable elements including cobalt, copper, nickel, manganese, lithium and others. A growing amount of used manganese containing materials in the battery cathode [2], will lead to increasing concentrations of manganese present in the high temperature smelter slag. In order to optimise the recycling process of these metals, accurate information is required on the phase equilibria in the Al2O3-CaO-Li2O-“MnO”-SiO2 system.

The battery smelter slag is a multi-component system containing alumina from the battery cases, silica and lime from fluxes, and manganese and lithium from the electrode materials. The Al2O3-CaO-SiO2 system is well known, therefore a phase equilibria study was performed on the quaternary “MnO”-Al2O3-CaO-SiO2 system. Discrepancies were identified between different studies [3-7] in the “MnO”-Al2O3-SiO2 ternary system. The present study accurately determined the phase equilibria in the ternary system “MnO”-Al2O3-SiO2 at metal saturation. Particular focus was given to the accuracy and reliability of the final results by highlighting the different reaction pathways, mass transfer mechanisms and reaction mechanisms taking place in the system, to enable improved design of kinetic and equilibration experiments and measurements in the “MnO”-Al2O3-SiO2 system. The quaternary system “MnO”-Al2O3-CaO-SiO2 has been studied by different authors [8-10], but no investigations were found at low constant “MnO”-concentrations.

The experimental procedures developed at the Pyrometallurgy Research Centre (PYROSEARCH) at The University of Queensland, were used, which involves equilibration of mixtures at high temperatures, rapid quenching, and accurate measurement of phase compositions using electron probe x-ray microanalyses. First, different reaction pathways in a closed system were analysed, which enable improved design of phase equilibrium experiments and measurements. Further experiments were undertaken to provide a more accurate phase diagram of the “MnO”- Al2O3-SiO2 system under alloy saturation. The result of this alternative phase diagram is shown in Figure 1A. Figure 1B shows the differences between the phase boundary lines of the previous studies and the present study.

Attention was given to possible reaction pathways in the slag phase as it approaches equilibrium. A typical microstructure of a slag sample treated with an oxidizing atmosphere, i.e. under CO/CO2 gas mixture, is shown in Figure 2. An unexpected “MnO” concentration profile was observed. A schematic presentation of the “MnO” concentration profiles is presented in Figure 3. This composition profile is unusual since MnO is higher in the area exposed to the gas phase although it is anticipated that manganese vaporization will occur. The following explanation for the observations is proposed. The fully-liquid slag layer
appears to be the result of oxidation of the alloy in the mixture by the gas phase. The following reaction pathway is proposed.

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\text{CO}_2 \text{ absorbed at the gas/slag interface provides a source of oxygen, where upon the oxygen is introduced into the liquid slag and transferred by diffusion from the gas/liquid interface into the bulk slag in the form of Mn}^{3+} \text{ and O}^{2-} \text{ due to the excess of oxygen present at the gas/slag interface. The diffusion of oxygen is accompanied the exchange between Mn}^{2+} \text{ and Mn}^{3+} \text{ ions in the slag. When the oxygen arrives at the alloy/slag interface, oxygen is adsorbed at the interface and the oxidation reaction to MnO takes place. The local “MnO” concentration in the slag is increased until all alloy is oxidised, the alloy/slag interface moves deeper into the sample and the thickness of the single liquid slag phase (zone 3) is increased. Simultaneously vaporization to manganese gas occurs at the slag/gas interface, leading to local concentration gradients on the vicinity of the gas/slag interface.}
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The work is being extended to the quaternary system “MnO”-Al\(_2\)O\(_3\)-CaO-SiO\(_2\) which closely resembles the future recycling industrial slags. Experiments are being undertaken in platinum metal envelopes. The slag reacts with the platinum foil and manganese is dissolved in the platinum. It has been previously demonstrated that the concentration of manganese in platinum alloy can be used to determine the oxygen partial pressure. The relationship between the oxygen partial pressure and the amount of Mn dissolved in Pt was investigated by Rao and Gaskell [12], and is shown in Figure 4. The effective oxygen partial pressure in the system will be derived using these Mn activity data in solid Pt alloy by direct
measurement of the Mn concentration in Pt and MnO activity coefficient values in slag taken from FactSage. Example of such “oxygen partial pressure” calibration curve for the MnO in slag of composition 11.6 wt.% Al₂O₃, 30.5 wt.% CaO, 42.4 wt.% SiO₂ and 15.5 wt.% MnO is given in Figure 5.

A comprehensive investigation of phase equilibria in the quaternary “MnO”-Al₂O₃-CaO-SiO₂ system is in progress.

![Figure 4: Thermodynamic data of Pt-Mn alloy and pure MnO solid [12]; experiment Mn concentrations in Pt](image)

![Figure 5: Relation between Pₒ₂ and wt.% Mn in platinum (FactSage calculations)](image)

References