Abstract

The major objective of the present research programme is to develop the beta-alumina based low-temperature sodium production process and to study the related electrochemical issues. Towards this end, the study begins with the investigation of some thermodynamic and transport aspects of the molten electrolyte, namely sodium tetrachloroaluminate (NaAlCl₄). The design, operation and evaluation of an electrochemical cell based on the process with specific reference to the role of anode material was the second objective of this study. More detailed evaluation of different types of carbon anodes in chloroaluminate melt with the aim of understanding their stability and electrochemical activity is the third objective of this work. The results obtained during the present investigation are presented in the following seven chapters in this thesis.

The first chapter provides some introductory information connected with the above electrochemical processes. This chapter begins with a description of the thermodynamics and transport properties of the chloroaluminate melts in general and sodium chloroaluminate in particular. A brief outline of the solid state sodium ion conductor, β - alumina, which forms the backbone of the present investigation is provided. The conventional sodium production process namely Downs process and the present β”-alumina based process are also introduced. The intercalation / de-intercalation behaviour of graphitic carbon materials which is responsible for many surface transformations and physical degradation in chloroaluminate melts is also outlined. This chapter ends with a brief statement of the specific objectives taken up in this research programme.

The experimental techniques employed and the specific experimental procedures adapted throughout the research programme are outlined in the second chapter. More specific experimental details adapted in individual research work are presented in their respective chapters.

The third chapter deals with the phase relations and thermodynamics of NaCl-AlCl₃ system. A careful construction of the phase diagram of NaCl-AlCl₃ system in the composition range 0.3 - 0.65 mol % AlCl₃ is reported. An important feature of this part of the work is the use of predominantly electrochemical methods namely, conductivity and emf measurements for the construction of the phase diagram.
melting points of the equimolar and eutectic compositions were determined by the conductivity and emf techniques respectively. The AlCl₃ liquidus was also determined by the conductivity method. The decomposition potentials of NaCl and NaAlCl₄ and their Gibbs energies of formation at a significantly low temperature of 423K were measured using a novel electrochemical technique involving electro-generated chlorine close-to-equilibrium conditions.

Chapter 4 presents some conductivity data obtained for NaAlCl₄ and compares them with similar data of LiAlCl₄ as well as KAICl₄ obtained under identical conditions up to a maximum temperature of 800K. Some of the conductivity data presented here for LiAlCl₄ and NaAlCl₄ are probably reported for the first time. A quartz conductivity cell, specially designed for electrical conductivity measurements of reactive molten salts at elevated temperatures, is also described. The resistivity of the large-sized $\beta''$- alumina tube used in the sodium production cell was obtained using DC polarisation measurements on reversible sodium / $\beta''$- alumina / sodium cell.

Chapter 5 deals with the main objective of the present research programme namely the technical assessment of the beta-alumina based low-temperature sodium production process and the design, assembly and operational evaluation of an electrolytic cell based on the process. The chapter begins with some comparative calculations of the two sodium production processes. Detailed description of the design and construction of a cell assembly in the new process is then provided. The operation of the cell using graphite and reticulated vitreous carbon (RVC) anodes are described. It is found that the former electrode disintegrate physically during electrolysis whereas the latter performs substantially better. The overall sodium production efficiency is determined as close to 100%. However, the anodic efficiency or the chlorine production efficiency is found to be substantially lower. This critical issue does form the basis for further studies on the carbon electrodes in the sodium chloroaluminate melt in the subsequent two chapters.

Chapter 6 presents the results of the electrochemical studies of graphite (rod and powder) by using the galvanostatic technique. The chapter begins with the analysis of graphite and RVC electrode materials anodically polarised in chloroaluminate melts. The hollow cylindrical graphite anode used in the sodium production cell showed significant volume expansion and physical damage which is attributed to the formation of C-AlCl₃-Cl graphite intercalation compounds (GIC).
Substantial surface exfoliation is noticed on graphite materials. The amorphous and fibrous RVC showed relatively lower surface exfoliation and damage. The GIC could be discharged or de-intercalated to generate chlorine and hence it is used as the cathode to configure a sodium-chlorine secondary battery. The capacity of graphite powder electrode for chlorine storage by intercalation and adsorption processes has been examined in this context. The capacity is influenced by the duration of charge, temperature and cycling. The intercalation / de-intercalation processes occurring in different carbon materials in basic, acidic and neutral chloroaluminate melts are also studied in greater detail using galvanostatic charge-discharge technique. These galvanostatic polarisation measurements clearly indicated the potential regions of intercalation / de-intercalation in the three melts. Thus it becomes possible to predict possible intercalation / de-intercalation processes and the composition of the GIC in the different chloroaluminate melts mentioned above.

Chapter 7 presents a detailed cyclic voltammetric study of different forms of graphite materials namely, graphite rod, graphite foil and graphite powder and vitreous carbons such as glassy carbon (GC) and RVC in the basic sodium chloroaluminate melt. Chlorine evolution is the only predominant anodic process on hard and compact glassy carbon electrode. On graphite, the electrochemical intercalation process, which is predominantly responsible for surface exfoliation and damage is initiated with the chlorine evolution at around +2.1V vs Al in NaAlCl₄ melt saturated with NaCl. On high surface area graphite powders, a chlorine adsorption / desorption redox process is also observed in the potential region of 1.2 – 1.6V. The importance of these processes on different carbon electrode materials and the influence of anodic potential limit, potential sweep rates, temperature and porosity are also presented and discussed in this chapter.

A brief summary and scope for further research work in this interesting area are also outlined at the end of this thesis.