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An electrochemical meter for measuring carbon potential in molten sodium

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ABSTRACT

Thermodynamic analysis and electrochemical investigations were carried out to evaluate the chemistry and electrode kinetics of a molten carbonate based electrochemical carbon meter for monitoring carbon in molten sodium. Based on the results of investigations a procedure was standardized for assembling the cell. The response of the cell thus assembled could be correlated to the carbon activity in sodium. Impedance studies established that mass transfer at iron membrane was the rate limiting step. Meters were extensively tested in both static and dynamic sodium for evaluating the stability and reproducibility in long term conditions.

1. Introduction

Liquid sodium is used as coolant in fast breeder reactors. Presence of non-metallic impurities like oxygen and carbon even in trace levels could lead to corrosion and mass transport in the coolant circuits [1]. Excess of dissolved carbon in sodium could lead to carburization [2–5] and result in deterioration of the mechanical properties of the structural steels. Different on line methods of measuring carbon in sodium had been developed [6–8]. Among these methods, measurement by a galvanic cell using molten carbonate electrolyte [8] is simple and significant since the measured parameter can be directly related to the chemical potential of carbon in sodium by the Nernst equation.

Reported results of measuring carbon activity using these molten carbonate based electrochemical cells are not encouraging [9–11]. Problems such as mixed potential due to parasitic reaction, often resulting in whisker growth and deposition of carbon, drift in potential due to instability in the reference electrode, need for long period of equilibration and disagreement between the measured carbon activity and the expected value were encountered. And the cells had poor life time. Different methods have also been suggested to overcome the problems associated with these cells [9]. Graphite, carburized iron, graphite packed iron [10] and graphite packed nickel tubes [11] had been used to overcome the problems associated with reference electrodes. In spite of these modifications, the experience with these meters was not satisfactory. Often the reference electrode graphite was cathode. This is in contradiction to the postulated reaction scheme wherein graphite is anode. We carried out a detailed thermo chemical analysis of molten carbonate electrolyte system to address these problems. Based on the results of this analysis, a suitable procedure to assemble the meter had been evolved. Electrochemical investigations of this system were carried out to understand the processes at the electrode-electrolyte interfaces. The results of all these studies are reported in this paper.

2. Theoretical background

The cell under investigation is a concentration cell of configuration given by (1).

$$\langle C_{\text{graphite}}\rangle|Li_2CO_3\text{–}Na_2CO_3|Fe|\{C\}_{Na} \quad (1)$$

C_{graphite} is the reference electrode and sodium with carbon dissolved in it acts as the indicator electrode and Li_2CO_3–Na_2CO_3 eutectic is the electrolyte.

Molten carbonates have a complex anion chemistry that can support many ionic species apart from CO_3^{2-} ion. It is known that oxygen gas dissolves in molten carbonates to some extent and its solubility data has been reported [12–14]. It is also known that dissolved oxygen exist as partly oxidized oxide as per reaction schemes given in Eqs. (2) and (3).

$$O^{2-} + (1/2)O_2 \rightarrow O_2^{2-} \quad (2)$$

$$O_2^{2-} + O_2 \rightarrow 2O_2^{-} \quad (3)$$

In the molten carbonate eutectic, O^{2-} ions can exist as Li_2O and Na_2O and peroxide ions as Li_2O_2 and Na_2O_2, while the super oxide can exist only as NaO_2 [15–17]. Other forms of oxides like sub oxide and per carbonate/peroxo carbonate are also known. They

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are observed as intermediates in reaction involving oxygen generation and are of transient in nature [18,19] and therefore are not considered in this discussion. Half cell reactions of the electrochemical cell involving different ionic species like oxide, peroxide, super oxide and carbonate can be represented by Eqs. (4)–(7):

$$C + (3/2)O_2 + 2e^- \Leftrightarrow {CO_3}^{2-} \quad (4)$$

$$2C + 3{O_2}^- + e^- \Leftrightarrow 2{CO_3}^{2-} \quad (5)$$

$$C + (3/2){O_2}^{2-} \Leftrightarrow {CO_3}^{2-} + e^- \quad (6)$$

$$C + 3O^{2-} \Leftrightarrow {CO_3}^{2-} + 4e^- \quad (7)$$

The reaction that predominates depends on the concentration of the reactant species (which in turn depends on the oxygen partial pressure in the gas phase over the electrolyte). Reaction scheme (4) involves direct reduction of molecular oxygen, with graphite playing the role of cathode. Existence of molecular oxygen in molten carbonate can happen in oxygen rich environment and in highly acidic melt only [20,21]. Reaction scheme (5) involves reduction of super oxide. Super oxide is observed in acidic melts only and, its concentration in basic melts with lithium cation is insignificant [22,23]. Predominance of the reaction schemes (4) and (5) can be identified by following the polarity of the graphite electrode. Reaction scheme (6) involves oxidation of carbon with participation of peroxide and in this case the graphite reference electrode would be anodic. Peroxide is known to exist in basic melt and it also requires moderately high oxygen pressures (cf Eqs. (2) and (3)). Reaction (7) is the oxidation of elemental carbon by O^{2-} ion. The reverse reaction (of (7)) namely the cathodic deposition of carbon during the electrolysis of molten carbonate has been observed on different electrodes. The deposition/oxidation are quantitative and reversible under certain conditions [24,25]. Among the above four reactions, scheme (7) is preferred to the other reactions. This is understandable as at high oxygen pressures required for other reactions undesirable direct chemical reaction between oxygen and carbon as well as iron membrane could occur leading to fall in oxygen partial pressure which in turn would alter the participating reaction scheme during the course of measurement. When the reaction scheme (7) predominates as the half cell reaction in the cell, activity of carbon in sodium sample a_C^{Na} can be related to the emf by the Nernst equation [26]:

$$E = \frac{(-RT/4F)}{\ln a_C^{Na}} \quad (8)$$

The important factors that govern the performance of the cell are (i) the availability of the reactant species of reaction scheme (7), namely O^{2-} ions in excess of other species and (ii) fast electrode kinetics. The former is dictated by the molten salt chemistry and the electrode kinetics is specific to the electrode. Kinetics is characterized by the exchange current density of the desired half cell reaction at the electrode interface. Both the parameters can be evaluated semi empirically as would be seen in the following sections.

It is reasonable to assume that the overpotential η associated with potentiometric measurement is a combination of activation overpotential η_a and concentration overpotential η_c as given in Eq. (9). Factors inherent in the chemical system do set a limit on the performance of the cell and they are addressed:

$$\eta = \eta_c + \eta_a \quad (9)$$

In a complex reaction scenario such as the molten carbonate various competing species try to establish the electrochemical equilibrium. Each electroactive species competes with the other species present in the electrolyte and therefore the concentration of the desired species needs to be higher than that of the other partly oxidized oxide species and the inadvertent impurity level present in the salt. While the molten salt chemistry dictates the extent of availability of the electroactive species, purity of the starting materials dictates the concentration of the impurities that can interfere in the measurement. It is possible to analyze the requirement as follows.

If it is also assumed that the process is governed by diffusion alone, and that the diffusion coefficients of all the electroactive species including the impurities are of the same order, the competition among the species could be quantified in terms of the limiting current of the respective species. Limiting current density I_L of a species is given by (10).

$$I_L = \frac{nFDC}{\delta} \quad (10)$$

In Eq. (10) n and F have their usual meanings. C is the concentration in mol cm^{-3} and δ is the Nernst layer thickness in cm.

Assuming the impurity level to be of the order of micromoles per liter and using a Nernst layer thickness (δ) of 0.01 cm [27] and a diffusion coefficient, $D = 10^{-6}$ cm^2 s^{-1} [22] and a typical value of $n = 2$, the limiting current density due to impurity is calculated to be 10^{-8} A/cm^2.

The reaction kinetics is specific to the electrochemical equilibrium at the electrode–electrolyte interface. There is no straight forward method to predict a lower limit for exchange current density. It is reasonable to assume that at least a monolayer of the electroactive species should be renewed on the surface of the electrode every 1 s for reproducible potential to develop. This works out to an exchange current density of 10^{-10} A cm^{-2} [28].

The exchange current density reported has a wide range varying from 10^{-2} A cm^{-2} to 10^{-10} A cm^{-2}. With the availability of commercial measuring instruments drawing current of the order of 10^{-14} A the kinetic requirement appears to be least demanding.

Thus when the chemical and the kinetic and the electrical requirements are considered together, the chemical aspects limit the performance as the later aspects are less demanding on the system.

For the reaction scheme (7) to dominate and establish the electrochemical equilibrium, the limiting current density due to O^{2-} species should be at least of the order of micro amperes, i.e. two orders higher than I_L due to impurities. The saturated oxide concentration in Li_2CO_3–Na_2CO_3 eutectic at 923 K had been evaluated to be 5.7 μmol cm^{-3} by impedance spectroscopy [29]. The O^{2-} concentration evaluated by other techniques is also of the same order [30]. It may be noted that the solution of O^{2-} in other eutectics with higher alkali metal carbonates is of higher order [31]. There is therefore reason to assume that the solubility in the Li_2CO_3–Na_2CO_3 eutectic is approximately 5 μmol cm^{-3}. In the following section the conditions that favor the desired concentration of oxide are evaluated and the kinetics of the electrode reaction is measured. Formation equilibria involving these species are given in Eqs. (11)–(15). As seen from these equilibria, the activities of the various oxide species are dependent upon the oxygen partial pressure over the electrolyte. Using the Gibbs free energies of these reactions [32,33], it is possible to compute the activity of different species in the electrolyte at different oxygen pressures at a chosen temperature. Considering the fact that the energy involved in the dissolution of the oxides in the melt is low and that the data are not available solid state values are used in the evaluation.

$$Li_2O + \langle C \rangle + O_2 = Li_2CO_3 \quad (11)$$

$$Na_2O + \langle C \rangle + O_2 = Na_2CO_3 \quad (12)$$

$$Li_2O_2 + \langle C \rangle + (1/2)O_2 = Li_2CO_3 \quad (13)$$

$$Na_2O_2 + \langle C \rangle + (1/2)O_2 = Na_2CO_3 \quad (14)$$

$$2NaO_2 + \langle C \rangle = Na_2CO_3 + (1/2)O_2 \quad (15)$$