A New Electrochemical Carbon Meter for Monitoring Carbon Activity in Liquid Sodium

P.R. Reshmi , T. Muthu Ambika , Rajesh Ganesan, V. Jayaraman* , R. Sridharan
Materials Chemistry & Metal Fuel Cycle Group, Indira Gandhi Centre for Atomic Research, Kalpakkam603102,India
* V. Jayaraman, vjram@igcar.gov.in

Abstract:

Liquidsodiumisusedascoolantinfastbreederreactors.Carbonisanimportantconstituentofsteels. The carbon atoms can readily diffuse across sodium-steel interfaces in sodium loops of fast breeder reactors. The carbon activity difference between the structural steel and sodium can lead to carburisation or decarburisation of structural steels. In order to monitor the carbon activity in liquid sodium, a compact electrochemical carbon meter (ECCM) has been developed. The performance of the meter was tested in static sodium at 848 to 998 K. The chemical activity of carbon determined was compared with the results obtained by equilibration studies.

Keywords: Carbon activity, liquid sodium, fast breeder reactors, electrochemical meter

1. Introduction

Fastbreeder nuclear reactorsuse sodium as coolant. Presence of non-metallic impurities like oxygen and carbon evenintrace levels could lead to corrosion and masstrans portincoolant circuits[1]. Carbonisanim portant constituen tofsteels. The carbonatom scan readily diffuse across sodium-steelinter facesin sodium loop soffast breed erreactors. Inapoly the rmalloop diss olution can occur at high temperatures and deposition can occur at lower temperatures leading to carburisation and decarburisation of steels, respectively. Excess of dissolved carbon in sodium could lead to carburization and result in deterioration of the mechanical properties of the structur alsteels[2]. The reforeiti simportant tomonitor the carbonactivity in liquid sodium. Different online methods of measuring carbon in sodium had been developed [3]. Online carbon meters were developed based on two different principles (i) diffusion flux devices and (ii) electrochemical devices. In diffusion flux devices, the concentration of carbon in the carrier gas, the flux across the probe wall and carbon activity with whichitisine quilibriu miscalculated. This method need scalibration and the detection and measuring system siscomplex. On the other hand, measurement by electrochemical cell using moltencar bonateelectrolyte[4] issimple and the measure demfcanbe directly related to carbonactivity by the Nernste quation. It isaconcentration cell of configuration

$$C_{graphite} / Li_2CO_3 - Na_2CO_3 /Fe/C_{Na} \quad (1)$$

Half cellreaction:

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

the activity of carbon in sodium a_{CNa} can be related to emf by Nernst equation

$$E=(-RT/4F)\times \ln a_{CNa} \quad (3)$$

A compacte lectrochemical carbonmeter(ECCM) with chemically bonded ceramictometal seal feed through with zero length flange was used in this new design which makes the assembly of the meter simpler. The details regarding assembling and testing of ECCM are discussed in thispaper.

2. Experimental

2.1 Preparation of electrolyte

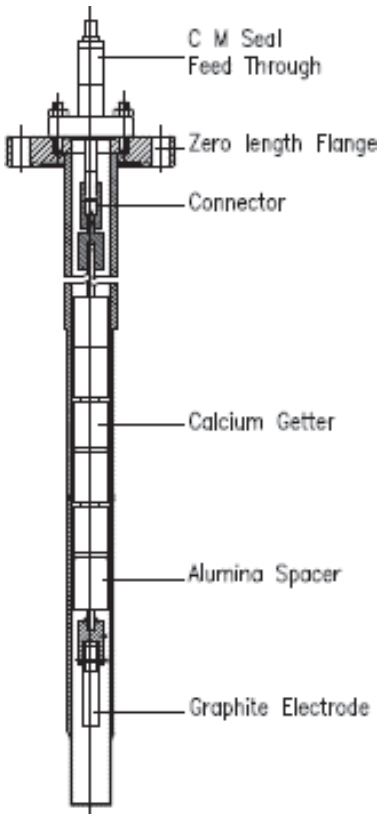
The electrolyte used in the ECCM is a mixture of lithium carbonate and sodium carbonate. Sodiumcarbonate (GRgrade,M/s Sarabhai

MChemicals, India) and lithium carbonate (AR Grade, M/s BDH, England) was prepared by fusing the 1:1 mol% of the component salts in an alumina crucible at 873 K for 6 h under CO_2 atmosphere. The mixture was then cooled and ground with amortar and pestlein an argonat mosphere glovebox. This purified mixture was used to assemble themeter.

2.2 Construction of meter

The schematic of the new design ECCM is given in Fig.1. A thin walled iron thimble forms the probe. The iron thimble part of the meter is made of high purity iron (C<0.03%) and welded to astainless steelpipe. This pipe as sembly was weld edtoakni feed gedflange having one side CF16 and other side CF35 flange (zero length flange) present at the top of the stainless steel pipe. This type of provision enables comfortable introduction of the reference electrodeinto the moltencar bonateel ectrolyte containe diniron thimble. Earlier ECCMs[5,6] were assembled having welding of M4 bolt to the CF16 flange, which led to difficulty during introducing the graphite electrode inside the molten electrolyte. In this new design ECCM, CF16flange has aninternal M4 thread so that ceramicto metal sealfeed through can be easily aligne dandtightened using M4 boltun dermoltencondition.The reference electrodeisa high purity graphite rod of 6 mm diameter attached to a ceramic to metal seal with the help of suitable connector. Three perforated stainless steel capsules containing coarse calcium granules were accommodated in between the alumina sleeves to maintain low oxygen partial pressure in the gas phase over the electrolyte. About 11 gofthe car bonateel ectrolyte was first taken inside the iron thimble of the meter. When the electrolyte was molten, the graphite electrode was slowly introduced inside the electrolyte, matching to the holes of the bottom CF16 matting flange. The whole assemblywas allowed to get cooled and later removed and tested in static sodium. The meters were tested in distilled sodium taken in a one end closed alumina tube. Annealed foils of SS316 of 100 μm thickness (source) as well as high purity nickel foils of purity 99.99% and 150 μm thickness (M/s Goodfellow Metals, UK) were also kept immersed in sodium during the equilibration and emf measurements. The equilibration experiments continued for more than 1500 h from 848 K to 998 K during which the cell output was measured continuously. At the end of the experiments, the SS and nickel foils were retrieved from sodium and analyzed for their carbon content using Eltra CS-800 analyser, Germany.

Fig.1. Schematic of new design electrochemical carbon meter



2. Results andDiscussion

New design ECCM was tested in static sodium for temperature response and long term stability. Temperature cycling was carried out from 848 K to 998 K. In order to get a stable output from the meter, meter was maintained for 100 h at each temperature. The calcium getter incorporated in the meter helped in attaining the desired output. Fig.2 shows the responseof ECCM to temperature variation instatic sodium experiments.The carbonactivity arrived from the meter out put response to temperature variation in static sodium is given in Table1. The nickelf oile quilibrated insituin sodium was analysed for its carboncontentand carbon activity was evaluated using the literature data on solubility of carbon in nickel [7]. Foile quilibration measurement was use dasatool for calibrating on linemeters.

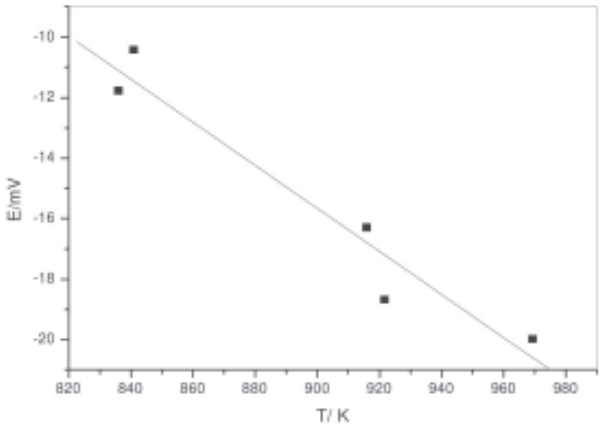


Fig.2. Response of ECCM to temperature variation in static sodium, standard deviation **= ± 1.2 mV**

Table1: Carbon activity arrived from meter response to temperature variation instatic sodium

S.NO.	Temp (K)	Emf (mV)	aCNa	aCNi
1.	836	-11.78	0.52	-
2.	841	-10.42	0.56	-
3.	916	-16.3	0.44	-
4.	922	-18.68	0.39	-
5.	970	-19.99	0.38	-
6.	973	-35	0.18	0.14
7.	998	-40	0.15	0.12

It can be seen from the table, the carbon activity determined by ECCM is comparable to that of the foil equilibration experiments.

4. Conclusions

A new design compact electrochemical carbon meter was assembled using a systematic assembling procedure. The response of electrochemical cell employing lithium carbonate- sodium carbonate electrolyte with graphite reference electrode is found to be reproducible during temperature cycling from 848 K to 998 K and having long term performance for a period of ~1500 h. The obtained carbon activity by ECCM is compared with foil equilibration studies.

5. References

1. P. Roy, G.P. Wozaldo, Nucl. Technol. 10 (1971)307.
2. K. Natesan, T.F. Kassner, J. Nucl.Mater. 37 (1970)223.
3. S. R. Pillai and C.K. Mathews, J. Nucl. Mater. 137 (1986)107.
4. F.J. Salzano, L. Newman, M.R. Hobdell, Nucl. Technol. 10 (1971)335.
5. S. R. Babu, P.R. Reshmi, T. Gnanasekarn, Electrochimica Acta 59 (2012)522.
6. R.Ganesan, V.Jayaraman, S.R.Babu, R.Sridharan, T.Gnanasekaran, J.Nucl.Sci. Tech. 48 (2011)483.
7. J.J. Lander, H.E. Kern, A.L. Beach, J.Appl. Phy. 23 (1952)1305.