Short communication

Spectrophotometric study of the corrosion behaviour of chromium in molten alkali carbonates

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Abstract

The corrosion of chromium species in molten $(Li/K)_2CO_3$ and $(Li/Na/K)_2CO_3$ are investigated by spectrophotometry. A strong charge-transfer absorption band is observed in the ultraviolet region with $\lambda_{max} = 372$ nm, and the molar absorptivity of CrO_4^{2-} in molten $(Li/K)_2CO_3$ is calculated. The corrosion rates are investigated by means of increasing the concentration of CrO_4^{2-} in the melts. Under an air atmosphere, the corrosion rate is slower in molten $(Li/K)_2CO_3$ than in molten $(Li/Na/K)_2CO_3$ and Cr_2O_3 corrodes more easily in molten $(Li/K)_2CO_3$ than Cr. With an atmosphere of $CO_2 = 1$ atm, there is no increase in the CrO_4^{2-} concentration in the solution phase during a period of 5 h. © 1998 Elsevier Science S.A.

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1. Introduction

Molten alkali carbonates have been investigated because of their considerable importance in the development of high-temperature fuel cells. A molten carbonate fuel cell (MCFC) is an energy-conversion device which converts the chemical energy of fuels (e.g., natural gas, hydrogen) directly into electricity. One of the serious problems in MCFC operation is the corrosion of the electrode and the current-collector [1–4], since such action significantly degrades cell performance.

Chromium is considered to be an important alloying element in obtaining corrosion protection in molten carbonate. Vossen et al. [5] have reported the electrochemical behaviour of chromium in molten carbonate mixtures by investigation with quasi-stationary polarization curve measurements and cyclic voltammetry. He also reported that in the potential image of the MCFC anode (viz., −1070 to −900 mV), the passivating properties of the oxide film improve when the material is polarized. Nevertheless, since the conductivity of the oxide film is probably still considerable, the use of a chromium coating as a MCFC anode current-collector would be limited. Ota et al. [6] investigated, by TGA experiments, the high-temperature corro-

sion of chromium in the presence of a carbonate melt in a CO_2–O_2 atmosphere. It was reported that hot corrosion occurs at 923 K with a $(Li_{0.62}K_{0.38})_2CO_3$ coating in O_2-containing atmosphere by the formation of liquid chromate. Hsu and Devan [7] disclosed the phase diagram of Cr–Li–K–C–O system at 650°C and established the phase stability diagrams by thermodynamic calculations.

In the study reported here, the corrosion behaviour of chromium in molten carbonate mixture is studied by spectrophotometric method.

2. Experimental

Reagent grade Li_2CO_3, Na_2CO_3 and K_2CO_3 powders were used. The experiments were performed with two different eutectic mixtures, namely, 62 mol% Li_2CO_3 + 38 mol% K_2CO_3 and 43.5 mol% Li_2CO_3 + 31.5 mol% Na_2CO_3 + 25 mol% K_2CO_3. The eutectic composition of $(Li/K)_2CO_3$ and $(Li/Na/K)_2CO_3$ was obtained by ball milling the powders for 72 h. Eutectic mixtures were dried at 200°C for 24 h prior to experiment.

Since the surface of quartz is blurred by the reaction with molten alkali carbonates, a new sapphire cell was designed with a 9.25×10^{-1} cm path length. A schematic diagram of the cell is given in Fig. 1. The upper side of the
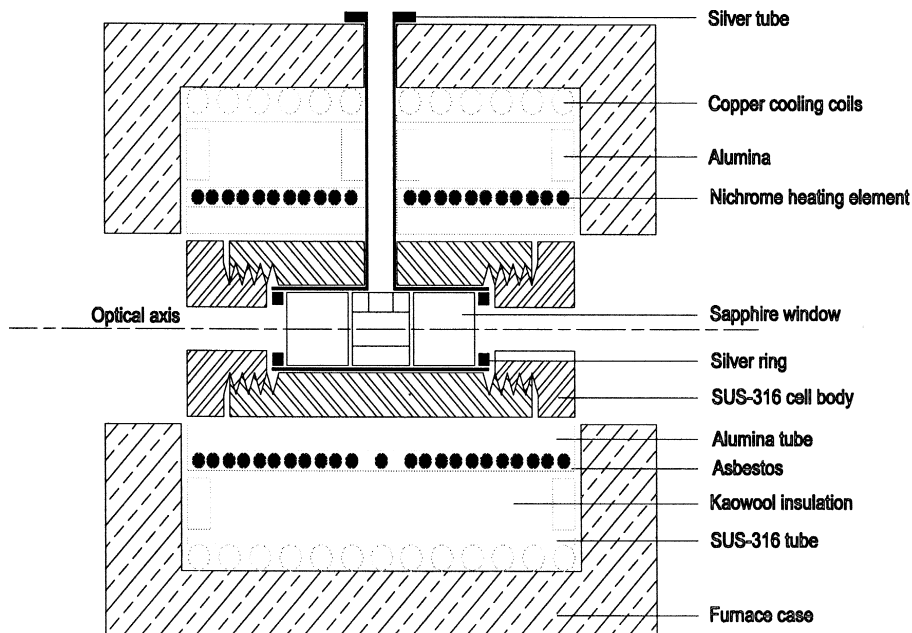
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Fig. 1. Schematic diagram of high-temperature sapphire cell for molten carbonates.

cell was fitted with a tube so as to control the gas condition. Spectra were measured using a Hewlett–Packard HP8452A UV–VIS spectrophotometer with a photo-diode array. Digitized data were collected at wavelength intervals of 2.0 nm. The temperature was maintained at 923 ± 5 K. This fluctuation in temperature exerted a negligible effect on absorption measurements. The complete experimental apparatus is shown schematically in Fig. 2.

To determine the molar absorptivity of CrO_4^{2-} in molten carbonate, the absorption spectra of K_2CrO_4 in molten carbonate were obtained and the concentration of chromium was determined by ICP-mass spectroscopy. The molar absorptivity of CrO_4^{2-} was calculated from the Beer–Lambert law.
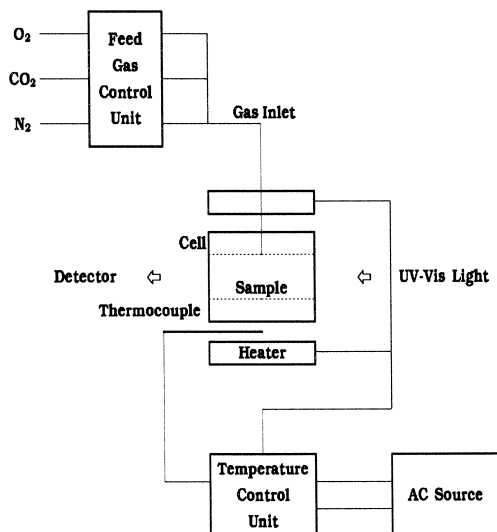
The spectra of CrO_4^{2-} in molten carbonate were recorded under two gas conditions; open to air and $P_{CO_2} = 1$ atm. The molten carbonate spectra were taken as a blank and then 0.001 g of Cr powder or 0.0005g of Cr_2O_3 powder was added to the cell so as to make the ratio of Li/K to Cr approximately 100:1. Next, the raw spectra of CrO_4^{2-} in the molten carbonates were obtained. The composition of the melts, the Cr species and the gas conditions are given in Table 1.

3. Results and discussion

The spectrum of CrO_4^{2-} in a molten Li/K = 62/38 mixture at 923 K is shown in Fig. 3. A strong absorption band is present in the ultraviolet region, with $\lambda_{max} = 372$ nm. The transition in CrO_4^{2-} is a type of charge-transfer, i.e., an electron transfer from a non-bonding orbital of an oxygen atom to the chromium. The spectra of CrO_4^{2-} in other molten salt media were reported in the 1960s by Smith and Boston [8]. In this study, the calculated molar absorptivity in molten $(Li/K)_2CO_3$ at 372 nm was about 10,000. This value is higher than those obtained in other molten salts.

Fig. 2. Schematic diagram of electronic absorption spectroscopy system.

Table 1
Composition of melts and chromium species and gas conditions

Melt composition	Added chromium species	Gas conditions
$(Li_{0.62} + K_{0.38})_2CO_3$	Cr	open to air
$(Li_{0.62} + K_{0.38})_2CO_3$	Cr	$p_{CO2} = 1$ atm
$(Li_{0.62} + K_{0.38})_2CO_3$	Cr_2O_3	open to air
$(Li_{0.435} + Na_{0.315} + K_{0.25})_2CO_3$	Cr	open to air
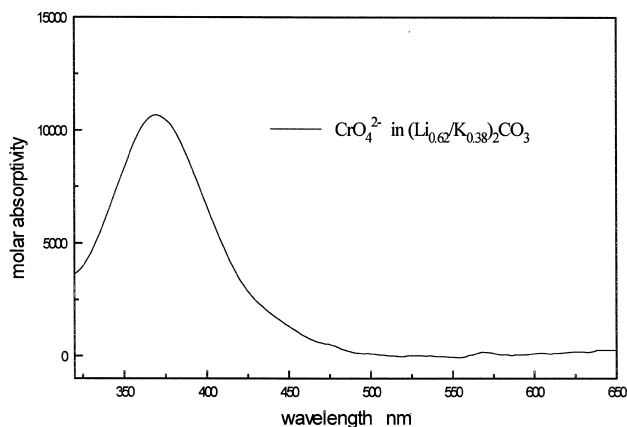
Fig. 3. Absorption spectrum of K_2CrO_4 in $(Li_{0.62}/K_{0.38})_2CO_3$ eutectic mixture at 923 K.

Fig. 5. Plots of CrO_4^{2-} absorbance at 372 nm in various carbonates at 923 K under an air atmosphere.

According to the phase diagram reported by Hsu and DeVan [7], when the ratio (Li + K):Cr is 100:1, K_2CrO_4 is stable at 650°C in the region of log $a_{O_2} = 0$–2, log $a_{CO_2} = -5$–2. In an electrochemical study, Vossen et al. [5] continued the existence of CrO_4^{2-} in the solution phase. Therefore, the concentration of CrO_4^{2-} in molten carbonate is proportional to the degree of corrosion of the chromium.

The absorption spectra of chromium in molten $(Li/K)_2CO_3$ at 923 K under an air atmosphere is presented in Fig. 4. The absorption caused by CrO_4^{2-} increases with time after chromium powder is added, i.e., the concentration of chromium in solution is increased. When Cr_2O_3 is added to carbonates, the absorption peak develops very quickly under an air atmosphere. In 10 min, the absorption exceeded the detection limit. For chromium in molten $(Li/Na/K)_2CO_3$ under air, the absorption peak of CrO_4^{2-} also appears, but develops at a slower rate than that in molten $(Li/K)_2CO_3$. For $P_{CO_2} = 1$ atm, however, no absorption is found during 5 h.

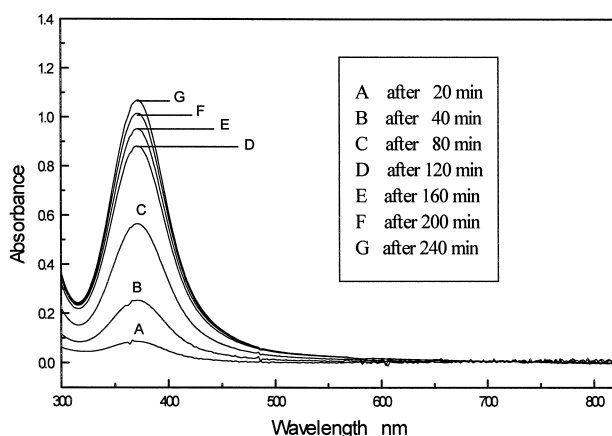The increase in absorption at 372 nm is plotted in Fig. 5. The corrosion rate of Cr_2O_3 in molten $(Li/K)_2CO_3$

under air is greater than that of chromium. The increasing rate of absorbance of chromium at 372 nm is slower in $(Li/Na/K)_2CO_3$. Ota et al. [6] explained the difference in the corrosion characteristics with the variation in the melt composition in terms of the melting point of chromate. The slower corrosion rate of chromium in molten $(Li/Na/K)_2CO_3$ may be explained in the same way. Because the melting points of Na_2CrO_4 and K_2CrO_4 are higher than that of Li_2CrO_4, in the K-, Na-rich region, a smaller amount of CrO_4^{2-} exists in the solution phase. Na_2CrO_4 is unstable, however, and has a lower melting point in the presence of water. This would provide an explanation for the data given in Fig. 6. The plot B in Fig. 6 is the absorbance of CrO_4^{2-} in insufficiently dried $(Li/Na/K)_2CO_3$. This contained 3% water at room temperature. In plot B, the absorbance decreased at about 25 min after chromium was added. Although the reason for this is not clear, it is a fact that the presence of water in molten carbonates affects the corrosion rate of chromium.

A comparison of the corrosion behaviour under different gas conditions is given in Fig. 7. Under $pCO_2 = 1$ atm, there is no increase in the absorbance at 372 nm during 5
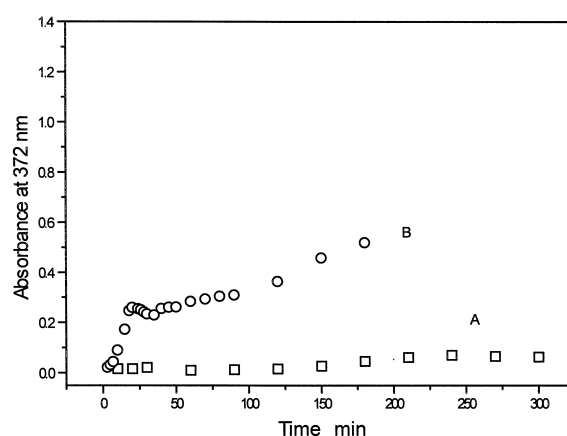

Fig. 4. Absorption spectra of chromium in $(Li_{0.62}/K_{0.38})_2CO_3$ eutectic mixture at 923 K with time.

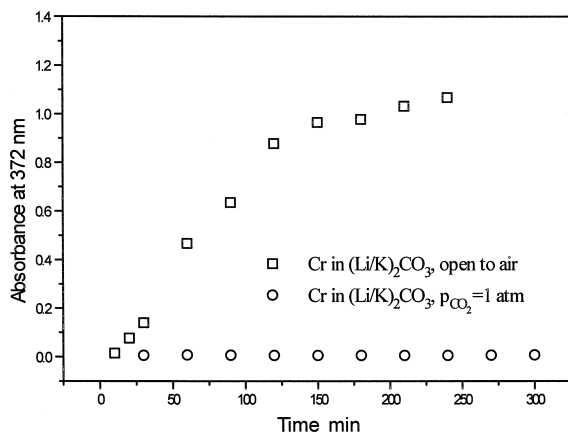Fig. 6. Plots of CrO_4^{2-} absorbance at 372 nm in: (A) $(Li/Na/K)_2CO_3$ dried at 200°C for 24 h; (B) insufficiently dried $(Li/Na/K)_2CO_3$.

Fig. 7. Plots of CrO_4^{2-} absorbance at 372 nm in $(Li_{0.62}/K_{0.38})_2CO_3$ at 923 K under different gas conditions.

h. Ota et al. [6] reported that the corrosion rate was roughly proportional to the oxygen pressure and Hsu and DeVan [7] reported that oxygen gas was the oxidant during the hot corrosion. The data shown in Fig. 7 provide a further proof of these observations.

Acknowledgements

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