Potentiometric Monitoring of Solution Chemistry for Corrosion Inhibition of Carbon Steel in Absorption Refrigeration Systems Masahiko Itoh^a, Kenji Machizawa^a, Hitoshi Yashiro^b, Ryo Ohmachi^b, Masaru Kawata^b and Naoaki Kumagai^b ^aHitachi Building Systems Co., Ltd., Tsuchiura, 300-0027 Japan ^bGraduate School of Engineering, Iwate University, Morioka, 020-8551 Japan

Absorption refrigeration systems, which utilize an extremely concentrated LiBr solution at temperatures up to ca. 433 K, require adequate control of concentrations of inhibitors to keep the construction materials free from corrosion damage^{1,2}. The concentrations of inhibitors in commercial machines are adjusted based on regular chemical analysis. Nevertheless, corrosion problems happen occasionally due to an unexpected change in solution chemistry. Therefore a continuous method is demanded to diagnose the corrosion in terms of solution chemistry. In the present study, the potential responses of Mo/MoO₂ and Fe electrodes to concentrations of hydroxide, molybdate, nitrate and dissolved oxygen in a LiBr solution were evaluated. These electrodes were selected because they can be inserted directly into the hot concentrated LiBr solution and no unfavorable contaminants should be released.

Mo/MoO₂ electrode was prepared by heating a Mo rod at 873 K in air and then reducing at 723 K under a hydrogen flow. The electrode was immersed into 2 or 17.3 mol kg⁻¹-H₂O (m) LiBr solution mixed with LiOH, Li₂MoO₄ and LiNO₃. The solution was deaerated with Ar. The potentials of Mo/MoO₂ and Fe were measured using an SCE held at ambient temperature. Some solutions were oxygenated by mixing oxygen into the Ar flow.

Fig. 1 shows the potential of Mo/MoO₂ electrode in the 17.3 m LiBr + 0.1 m LiOH + 10^{-2} m Li₂MoO₄ solution as a function of immersion time and temperature up to 428 K. The potential of Mo/MoO₂ was stable over the whole temperature tested. Fig. 2 shows the potential of Mo/MoO₂ electrode at 428 K as a function of concentrations of LiOH, Li₂MoO₄ and LiNO₃. The electrode responded to the concentration of LiOH but not to Li₂MoO₄ and LiNO₃. Similar results were also obtained at 428 K.

The potential of Mo/MoO_2 responded sharply to O_2/Ar ratio in the flowing gas in 2m LiBr solution and also in 17.3m LiBr solution though the response became less sensitive.

Fig. 3 shows an example of time variation of potential of Fe in the 17.3 m LiBr + 0.1 m LiOH + 10^{-2} m Li₂MoO₄ + z m LiNO₃ solution at 428 K. The potential of Fe became noble as the concentration of LiNO₃ increased. An anodic polarization curve indicated that the passivation and pitting potentials of Fe under this environment are about -600 and -450 mV. Nitrate ion helps Fe to passivate quickly but too much amount of it could cause pitting. Because Mo/MoO₂ is immune to the concentration of LiNO₃, it can be seen from the potential difference between Mo/MoO₂ and Fe whether the concentration of LiNO₃ is in an adequate level or not.

References

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Fig. 1 The potential of Mo/MoO_2 electrode in a 17.3 m LiBr + 0.1 m LiOH + 10^{-2} m Li_2MoO_4 solution as a function of immersion time and temperature.



Fig. 2 The effect of concentration of $\text{LiOH}(\circ)$, Li_2MoO_4 (\Box) and $\text{LiNO}_3(\Delta)$ on the potential of Mo/MoO₂ electrode. Solid symbols indicate the results in 17.3m LiBr at 393 K and open ones in 2 m LiBr at 353 K. The standard concentrations of LiOH, Li_2MoO_4 and LiNO_3 are 10^{-1} , 10^{-2} and zero, respectively.



Fig. 3 Effect of concentration of NaNO₃ on the potential of Fe in 17.3 m LiBr + 0.1 m LiOH + 10^{-2} m Li₂MoO₄ solution at 428 K.