

Cyclic Voltammetry of Fe, Ni, Cr, Co, and Mn ions in NaCl-MgCl₂ at 823 K

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1. Introduction

Molten salt reactors have been actively studied for their high thermal efficiency, safety, and economics. Chloride-based salts can be used in fast-spectrum molten salt reactors. However, as the high-temperature molten salt circulates through the structure, it has the possibility of reacting with the structural materials and producing corrosion products. Therefore, the control of these corrosion products is necessary for the utilization of chloride-based salts in molten salt reactors. This requires electrochemical investigations of the alloying elements responsible for the corrosion products in various environments. Electrochemical experiments have been performed on Fe, Ni, Cr, and Mn, which are the main alloying elements in iron-based or nickel based alloys used mainly as structural materials using cyclic voltammetry (CV).

2. Experimental

2.1 Chemiclals

All chemicals were stored and prepared under a high purity argon gas (99.999 %) environment in a glove box, with concentrations of oxygen and moisture kept at levels below 0.1 ppm. The eutectic of NaCl (99.99%, ultra dry, Alfa Aesar)-MgCl₂ (99.99%, ultra dry, Alfa Aesar) was prepared in 57:43 mol %. We used iron(II) chloride (FeCl₂, 99.99%, anhydrobeads, Sigma Aldrich), nickel(II) chloride (NiCl₂, 99.99%, anhydrous, Sigma Aldrich), chromium(III) chloride (CrCl₃, purified by sublimation 99%, Sigma Aldrich), manganese(II) chloride (MnCl₂, 99.99 %, anhydrobeads, Sigma Aldrich), cobalt(II) chloride (CoCl₂, ≥98.0%, anhydrous, Sigma Aldrich). All chlorides except iron(II) chloride were added to the eutectic at 0.1 Wt%, and iron(II) chloride was added at 0.5 Wt%.

2.2 Electrochemical cells and electrodes

A quartz tube (OD: 13 mm, ID: 10 mm) with one end closed round was used as the electrochemical cell. Tungsten wires (99.99%, Alfa Aesar) with a diameter of 1 mm were used as working, quasi-reference, and counter electrode. All electrodes were kept independent of each other with quartz guide tubes. All electrodes were polished with 800, 1000, and 1200 grit sandpaper and cleaned in an ultrasonic cleaner using ethanol, acetone,

and ultrapure water for one hour each. The electrodes were then dried in an oven at 120 degrees for over 12 hours. The electrochemical cell was prepared by the same ultrasonic cleaning step followed by drying.

2.3 Experimental method

All experiments were conducted in an argon environment in the glovebox with an electric furnace. The electrochemical measurement equipment was a VersaStat3 from Princeton Applied Research Inc. Cyclic voltammetry was conducted at 823 K with five steps of scan rate ranging from 0.05 V/s to 0.5 V/s.

3. Result and Discussion

Fig. 1 shows cyclic voltammograms of MnCl₂, CrCl₃, FeCl₂, CoCl₂, and NiCl₂ in NaCl-MgCl₂ on W electrode at 823 K. For NiCl₂ and MnCl₂, single oxidation-reduction peak pair was identified. Therefore, Ni(II) and Mn(II) ions have single reduction step. For FeCl₂ and CoCl₂, two oxidation-reduction peak pairs were observed. (Fig 1) That indicated that Fe(II) will be exist Fe(III). It is possible that the CoCl₂ was not high purity, so there could have been impurities mixed in. Three redox peak pairs were observed for CrCl₃. This indicate that Cr(III) could be reduced by following two step: Cr(III) to Cr(II) and Cr(II) to Cr(0).

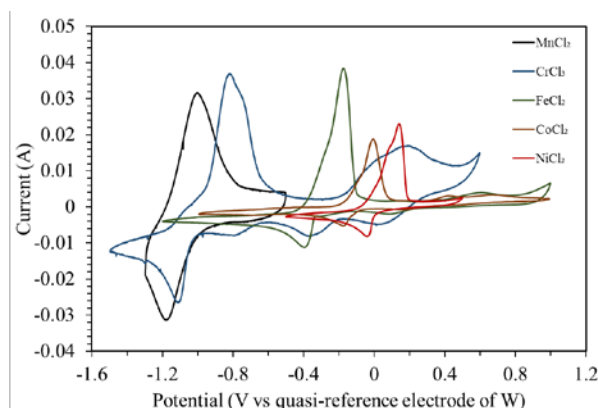


Fig 1. Cyclic voltammograms of MnCl₂, CrCl₃, FeCl₂, CoCl₂ and NiCl₂ in NaCl-MgCl₂ on W electrode at 823 K

Table I shows the potential window in which the ionic reaction exists and the average cathodic peak potential (vs quasi-reference electrode of W) at which the reduction reaction to metal occurs in each reaction. The average of these potentials was calculated from the sum

of the respective refresh rates.

Table I: The Average Value of Potential (V vs quasi-reversible electrode of W) at 823 K

	Reaction	The potential window	Potential(V)
FeCl ₂	Fe ²⁺ +2e ⁻ →Fe	-1.2 V~1.0 V	-0.3922
NiCl ₂	Ni ²⁺ +2e ⁻ →Ni	-0.5 V~0.5 V	-0.0390
CrCl ₃	Cr ³⁺ +3e ⁻ →Cr	-1.5 V~0.7 V	-1.1558
MnCl ₂	Mn ²⁺ +2e ⁻ →Mn	-1.3 V~-0.5 V	-0.9632
CoCl ₂	Co ²⁺ +2e ⁻ →Co	-1.0 V~1.0 V	-0.1636

The reduction reactions of Fe(II)/Fe(0), Cr(III)/Cr(0), Ni(II)/Ni(0), Mn(II)/Mn(0), and Co(II)/Co(0) were considered quasi-reversible by the slope of the cathode peak potential against the logarithm of the scan rate. The formal potential can be calculated from equation (1) for electrodeposition. Table II shows the formal potentials for each reduction reaction [1].

$$(1) E^{0'} = E_p - \frac{RT}{nF} \ln C_{M^{n+}} - 0.8540 \frac{RT}{nF}$$

In the equation, $E^{0'}$ is the formal potential, E_p is the cathodic peak potential, R is the universal gas constant, T is the temperature (K), n is the number of electrons, F is Faraday's constant, and $C_{M^{n+}}$ is the molar concentration.

Table II: The Formal Potential of FeCl₂, NiCl₂, CrCl₃, MnCl₂, and CoCl₂ at 823 K

	The formal potential (V vs quasi-reversible electrode of W)		
	Average	Min(scan rate)	Max(scan rate)
FeCl ₂	-0.2803	-0.2770	-0.2841
NiCl ₂	0.0776	0.0728	0.0767
CrCl ₃	-1.0610	-1.0421	-1.0762
MnCl ₂	-1.0483	-1.0375	-1.0705
CoCl ₂	-0.0496	-0.0376	-0.0592

4. Conclusions

To investigate main alloying elements in iron-based or nickel-based alloys used primarily as structural materials, the electrochemical behaviors of FeCl₂, CrCl₃, NiCl₂, MnCl₂, and CoCl₂ in molten NaCl-MgCl₂ were investigated at 823 K. W electrode was used as working electrode, quasi-reference electrode, and counter electrode. The oxidation-reduction behavior of each ion was confirmed by the CV data and the formal potential was calculated. The reversibility of the oxidation-reduction reaction as a function of scan rate was confirmed as a quasi-reversible system. If this experiment is combined with square wave voltammetry

and spectroelectrochemical experiments, it could be applied to the control of corrosion products.

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