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Effect of gluconate ions on electroreduction phenomena during manganese deposition on glassy carbon in acidic chloride and sulfate solutions

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ABSTRACT

Cathodic processes occurring during manganese deposition from acidic baths (pH 3.5) were investigated using glassy carbon rotating disk electrode. Cyclic voltammetry, linear sweep voltammetry and anodic sweep voltammetry were applied. Speciation and buffer capacities of chloride, chloride-gluconate, sulfate and sulfate-gluconate solutions were determined. Two ranges of the potentials (vs. Ag/AgCl) were considered: from −0.8 V to −1.56 V and below (up to −1.8 V) corresponding to hydrogen evolution and manganese deposition, respectively. In the chloride bath, strong adsorption of $MnCl^+$ on the cathode inhibited hydrogen evolution, favored fast metal nucleation and deposition of fine grained coatings, but low buffering action of the bath enhanced self-dissolution of manganese. Addition of gluconate improved buffer capacity of the bath, inhibited metal nucleation and hindered somewhat secondary metal dissolution, but the presence of chloride ions and low ammonium ions concentration resulted in the formation of hydroxide species as a secondary product of metal oxidation. Sulfate bath prevented manganese dissolution, but buffer effect of the solution was too small to stabilize pH at the cathode surface. The best buffering action of the sulfate-gluconate system originated from the cooperative action of gluconate and ammonium species made possible to obtain metallic layer protected from the dissolution by the electrolyte. Weak adsorption of $MnSO_4$ on the cathode in sulfate baths lead to the hydrogen evolution under limiting current in the potential range preceding manganese deposition. Independently on the bath composition, manganese started to deposit at approx. −1.56 ± 0.01 V (vs. Ag/AgCl) according to the instantaneous model of 3D nucleation. Average diffusion coefficients of the manganese species of order 10^{-6} cm^2/s were found.

1. Introduction

Manganese is the most electronegative metal able to electrochemical deposition from aqueous solutions. Typically, neutral or weak alkaline ammonium sulfate based baths are used [1–3]. These characterize with higher buffer capacity than chloride electrolytes preventing precipitation of manganese oxides/hydroxides at the cathode surface. The latter is caused by intensive hydrogen coevolution, especially when some contaminations are present in the bath. It relates mainly to iron, cobalt, nickel, copper, etc., i.e. more noble metals showing low hydrogen overpotentials [1]. Some inorganic additives are intentionally introduced to the solutions to increase current efficiency of manganese deposition. SO_3^{2-}, SeO_3^{2-} TeO_3^{2-} or SCN^- ions are reduced on the cathode producing adsorbates acting as a poison for hydrogen evolution [1,4–8]. Alternative organic additives (amines, paraformaldehyde, glycerol) [7] or non-aqueous solutions [9,10] as well as various electrolysis performances (pre-electrolysis, membrane reactor) [11,12] were also tested for the improvement of the process. It has to be noted that results of the electrochemical studies on the manganese deposition vary for different authors due to use solutions of different composition and purity or changed plating conditions.

The presence of additives affects the phase structure of manganese layers as well as decreases their purity. Cu, Ni, Co, Zn, etc. [1,13] and organic compounds [7] stabilize γ-Mn, VIB elements compounds enhance α-Mn formation [1,3], while amorphous deposits are obtained in the ionic liquids [9,10]. Crystal structure of manganese deposits is affected also by the substrate material (e.g. Pt, Fe, Cu) and current density [2]. It was observed, that γ-Mn is produced at low current densities, while an increase in the current leads to the formation of a mixture γ and α phases, and

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finally solely α-Mn is preferred at high overpotentials. It is worth to note that standard electrode potentials of both manganese modifications are very closed (α-Mn/Mn^{2+} −1.18 V, γ-Mn/Mn^{2+} −1.17 V). Metastable γ-phase can start to transform into α form already in a few hours after electrolysis, but duration of the phase transformation depends on the thickness and purity of the metal [1,3]. In fact, both crystallographic modifications of manganese are regular structures of different lattice parameters (α – A12, γ – A1).

A review of the literature has shown that enhanced manganese deposition can be obtained in the electrolytes of high purity and buffer properties or in the presence of additives. Therefore, the aim of this work was to investigate the influence of sodium gluconate as a buffering agent on the manganese deposition from acidic chloride and sulfate solutions. Sodium gluconate or gluconic acid are cheap and nontoxic compounds used usually as metal complexing agents in both alkaline and acidic solutions. Previous studies [14] have shown that the presence of sodium gluconate in acidic chloride-sulfate solution improved the quality of the Ni–Mn deposits. This work was carried out to give more insight into the role of gluconate ions during electroreduction of manganese(II) ions. Various electrochemical techniques were used for detailed investigations of the influence of the individual bath components as well as their combined effects on the course of the cathodic reactions. This allowed contributing to the understanding about the mechanism of the metal deposition, as no similar reports were published earlier.

2. Experimental

Electrochemical reduction of manganese ions was carried out from solutions containing 0.5 M Mn^{2+} as chloride or sulfate salt, 0.5 M H_3BO_3 and 0.5 M ammonium salt (chloride or sulfate, respectively). 0.2 M sodium gluconate was used as an additive. The pH of all baths was 3.5 ± 0.1. For comparison, some additional measurements were performed in the electrolytes deprived of the manganese salt or with 1 M Mn(II) as well as using 0.5 M Mn(II) baths with 0.5 M Na_2SO_4 instead of ammonium sulfate. Reagents of analytical purity (Avantor Performance Materials Poland S.A.) were used, without any additional purification procedure.

Equilibrium distribution of species in the baths was calculated according to the stability constants adopted from the literature and using HySS2009 free software.

Buffer capacities of the solutions were determined by slow addition (Crison titrator) of 0.1 M HCl or 0.1 M NaOH to the portion (20 cm^3) of the investigated electrolyte until appropriate pH (2.5 or 4.5) was achieved. Density and viscosity of the solutions were determined using glass pycnometer and Ostwald viscometer, respectively. Demineralized water was used as a standard solution (0.998 g/cm^3, 9.78×10^{-4} Pa s [15]).

Electrochemical measurements were carried out in a three-electrode cell. Glassy carbon rotating disk was applied as a working electrode (0.25 cm^2), a platinum plate (1 cm^2) as a counter electrode and an Ag/AgCl electrode as a reference electrode. All potentials in the further text are referred to this electrode. A few experiments were performed using gold, nickel and manganese substrates. Before each experiment working electrodes with a mirror finish were chemically cleaned in 1 M sulfuric acid, then washed in water and ethanol. Autolab potentiostat/galvanostat (PGSTAT30) controlled by a microcomputer was used.

Various electrochemical techniques were used. Cyclic and linear sweep voltammograms were registered at a potential scan rate of 20 mV/s. First sweep of CV and LSV was always performed from the initial potential of −0.8 V (vs. Ag/AgCl) toward more negative values. Stripping analysis was performed immediately after potentiostatic manganese deposition at various cathode rotation rates (0–1250 rpm) and at fixed potentials for 60 s, without removing the working electrode from the solution. Stripping curves were registered from deposition potentials up to −0.8 V at the potential scan rate of 20 mV/s (0 rpm) or 50 mV/s. Chronoamperometric curves of manganese deposition on GC (0 rpm) at various potentials were registered for 40 s. Potentiostatic deposition of manganese was carried out at −1.65V for 15 min in the stagnant baths. Morphology of deposited layers was observed under optical microscope (NIKON). 100 cm^3 of solution (not deareated) was used in each experiment. All experiments were performed at ambient temperature (21 ± 1 °C).

3. Results and discussion

3.1. Characteristics of solutions

Acidic chloride and sulfate solutions with or without sodium gluconate were used in this study. Manganese can exist in various soluble forms, i.e. as free Mn(II) ions or complexes. Speciation of the baths was examined using equilibrium diagrams calculated according to the equilibrium quotients and stability constants summarized in Table 1. It was found that chloride ($MnCl^+$, $MnCl_2$, $MnCl_3^-$) and sulfate ($MnSO_4$, $Mn(SO_4)_2^{2-}$, $MnHSO_4^+$) complexes as well as free Mn^{2+} ions are dominating manganese species in chloride and sulfate system, respectively. Various $Mn(OH)_m{}^{2-m}$ ($m = 1 \div 3$) and $Mn(NH_3)_n{}^{2+}$ ($n = 1 \div 4$) complexes can be also present, but they represent only minor fractions of total Mn(II) concentration (0.5 M). Distribution of the main metal species was practically independent on the presence of gluconate ions, since Mn–Glu complexes are stable solely in alkaline solutions [18,19],

Table 1
Equilibrium constants at 298 K [16,17].

Reaction	Equilibrium quotient	Constant
$Mn^{2+} + H_2O \leftrightarrow MnOH^+ + H^+$	$\beta_1 = \frac{[MnOH^+][H^+]}{[Mn^{2+}]}$	$\log\beta_1 = -10.59$
$Mn^{2+} + 2H_2O \leftrightarrow Mn(OH)_{2\ aq} + 2H^+$	$\beta_2 = \frac{[Mn(OH)_2][H^+]^2}{[Mn^{2+}]}$	$\log\beta_2 = -22.42$
$Mn^{2+} + 3H_2O \leftrightarrow Mn(OH)_3^- + 3H^+$	$\beta_3 = \frac{[Mn(OH)_3^-][H^+]^3}{[Mn^{2+}]}$	$\log\beta_3 = -34.81$
$Mn^{2+} + Cl^- \leftrightarrow MnCl^+$	$\beta_1 = \frac{[MnCl^+]}{[Mn^{2+}][Cl^-]}$	$\log\beta_1 = 0.607$
$Mn^{2+} + 2Cl^- \leftrightarrow MnCl_2$	$\beta_2 = \frac{[MnCl_2]}{[Mn^{2+}][Cl^-]^2}$	$\log\beta_2 = 0.041$
$Mn^{2+} + 3Cl^- \leftrightarrow MnCl_3^-$	$\beta_3 = \frac{[MnCl_3{}^-]}{[Mn^{2+}][Cl^-]^3}$	$\log\beta_3 = -0.305$
$Mn^{2+} + SO_4^{2-} \leftrightarrow MnSO_4$	$\beta_1 = \frac{[MnSO_4]}{[Mn^{2+}][SO_4^{2-}]}$	$\log\beta_1 = 2.25$
$Mn^{2+} + 2SO_4^{2-} \leftrightarrow Mn(SO_4)_2^{2-}$	$\beta_2 = \frac{[Mn(SO_4)_2^{2-}]}{[Mn^{2+}][SO_4^{2-}]^2}$	$\log\beta_2 = 1.87$
$Mn^{2+} + HSO_4^- \leftrightarrow MnHSO_4^+$	$\beta_3 = \frac{[MnHSO_4^+]}{[Mn^{2+}][HSO_4^-]}$	$\log\beta_3 = 2.26$
$Mn^{2+} + 2HGlu^- \leftrightarrow MnGlu_2 + 2H^+$	$K = \frac{[MnGlu_2][H^+]^2}{[Mn^{2+}][HGlu]^2}$	$\log K = -16.48$
$Mn^{2+} + NH_3 \leftrightarrow Mn(NH_3)^{2+}$	$\beta_1 = \frac{[Mn(NH_3)^{2+}]}{[Mn^{2+}][NH_3]}$	$\log\beta_1 = 0.908$
$Mn^{2+} + 2NH_3 \leftrightarrow Mn(NH_3)_2^{2+}$	$\beta_2 = \frac{[Mn(NH_3)_2^{2+}]}{[Mn^{2+}][NH_3]^2}$	$\log\beta_2 = 1.38$
$Mn^{2+} + 3NH_3 \leftrightarrow Mn(NH_3)_3^{2+}$	$\beta_3 = \frac{[Mn(NH_3)_3^{2+}]}{[Mn^{2+}][NH_3]^3}$	$\log\beta_3 = 1.58$
$Mn^{2+} + 4NH_3 \leftrightarrow Mn(NH_3)_4^{2+}$	$\beta_4 = \frac{[Mn(NH_3)_4^{2+}]}{[Mn^{2+}][NH_3]^4}$	$\log\beta_4 = 1.53$
$H^+ + HSO_4^- \leftrightarrow H_2SO_4$	$K = \frac{[H_2SO_4]}{[H^+][HSO_4^-]}$	$\log K = 1.12$
$H^+ + Glu^- \leftrightarrow HGlu$	$K = \frac{[HGlu]}{[H^+][Glu^-]}$	$\log K = 3.56$
$H^+ + NH_3 \leftrightarrow NH_4^+$	$K = \frac{[NH_4^+]}{[H^+][NH_3]}$	$\log K = 9.23$
$H^+ + H_2BO_3^- \leftrightarrow H_3BO_3$	$K_1 = \frac{[H_3BO_3]}{[H^+][H_2BO_3^-]}$	$\log K_1 = 10.73$
$2H^+ + HBO_3^{2-} \leftrightarrow H_3BO_3$	$K_2 = \frac{[H_3BO_3]}{[H^+]^2[HBO_3^{2-}]}$	$\log K_2 = 13.26$
$3H^+ + BO_3^{3-} \leftrightarrow H_3BO_3$	$K_3 = \frac{[H_3BO_3]}{[H^+]^3[BO_3^{3-}]}$	$\log K_3 = 14.20$
$NH_3 + HSO_4^- \leftrightarrow NH_4SO_4^-$	$K = \frac{[NH_4SO_4^-]}{[NH_3][HSO_4^-]}$	$\log K = 1.030$