

Article

Properties and Corrosion Resistance of Manganese Electrodeposits Obtained from Sulfate Bath at Different Temperatures in Presence of Tellurate(VI) Additive

Vasaris Statkevičius *, Egidijus Griškonis  and Nerita Žmuidzinavičienė

Department of Physical and Inorganic Chemistry, Faculty of Chemical Technology, Kaunas University of Technology, Radvilėnų Str. 19, 50254 Kaunas, Lithuania; egidijus.griskonis@ktu.lt (E.G.); nerita.zmuidzinaviciene@ktu.lt (N.Ž.)

* Correspondence: vasaris.statkevicius@gmail.com

Abstract

As a chemical element, manganese is used in a wide range of industries, particularly steelmaking and creating alloys and as a sacrificial coating for corrosion protection. Electrodeposition is a low-energy process; however, manganese electrodeposition from aqueous solutions remains challenging due to the highly negative reduction potential of Mn^{2+} . The addition of group VI elements such as selenium, sulfur or tellurium to the electrolyte improves both coating quality and the current efficiency of manganese electrodeposits by suppressing the competing hydrogen evolution reaction (HER). While selenium and sulfur compounds are widely studied electrolyte additives, research on the use of tellurium additives in the electrolyte and their influence on the manganese electrodeposition process and subsequent coating properties remains limited. In this work, manganese electrodeposits were obtained from a manganese ammonium sulfate bath (MASB) electrolyte with a sodium tellurate(VI) additive at both room and elevated temperatures. The resulting coatings, which also underwent a phosphating process to enhance the corrosion resistance of the coating, were investigated for properties such as morphology, elemental composition, and corrosion resistance; all corrosion tests were carried out in a 3% NaCl solution. The findings show that coatings deposited at higher temperatures exhibit a more compact surface structure, with α -Mn becoming more abundant as the MASB temperature increases. Furthermore, higher-temperature deposition produces coatings with greater current efficiency, though at the cost of a higher concentration of incorporated tellurium. Finally, the coatings that underwent the phosphating were evaluated against untreated (uncoated and non-phosphated) mild carbon steel regarding their corrosion resistance.

Keywords: manganese coatings; phosphating; corrosion; Te additive



Academic Editors: Haiyan Li and Yexiang Cui

Received: 3 June 2026

Revised: 26 June 2026

Accepted: 30 June 2026

Published: 4 July 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

In terms of global demand, manganese is the fourth most consumed metal in the world. It is widely used in electronic components, stainless steel processing, military applications [1], the production of non-ferrous and many steel alloys, and as a sacrificial coating in order to prevent corrosion. The processing of manganese deposits is mainly carried out via pyrometallurgy [2] and hydrometallurgy [3].

Manganese electrodeposition faces challenges due to the highly negative reduction potential of manganese ($E^0 = -1.18$ V vs. SHE) [4]. This standard potential results in low current efficiency, i.e., ineffective electrodeposition that results in very thin coatings and

prolonged deposition times. The most widely used electrolytes for the electrodeposition of manganese coatings are chloride- or sulfate-based solutions [5], typically containing MnSO_4 and $(\text{NH}_4)_2\text{SO}_4$ or MnCl_2 and NH_4Cl salts. Anode selection depends directly on the chosen electrolyte: graphite is utilized in a chlorine-based medium, whereas Pb and Pb-1%Ag alloys coated with lead(IV) oxide are used in a sulfate medium. A sulfate medium is frequently preferred to avoid the environmental and safety hazards of the chlorine gas that is generated during the electrodeposition. The ammonium salts formed in the electrolyte act as a buffer within the MASB solution, maintaining pH values around 2–3.5 and 6–7. Performing electrodeposition at a lower pH is advantageous as it facilitates the dissolution of sodium tellurate, notably, with the addition of sulfuric acid. A mixture of manganese sulfate, ammonium sulfate, and sodium tellurate maintains a pH of approximately 5. Theoretically, manganese electrodeposition can be further enhanced by controlling the surface of the substrate [6]. By displacing most of the water from the substrate and replacing it with a thin layer of polymers or hydrogels, HER can be suppressed while allowing a more effective deposition. However, a key challenge lies in developing polymers or hydrogels that can withstand elevated electrolyte temperatures and resist degradation in highly acidic media. This limitation can be circumvented by replacing polymer-based membranes and hydrogels with more chemically stable aligned carbon nanotube array membranes that can even further influence selectivity by generating symmetrical redox currents [7]; i.e., cation-selective multichannel membranes (CSMM) can selectively modulate ion transport at the electrode interface. By utilizing this selectivity, only preferable ions such as Mn^{2+} can pass through, thereby electrodeposition, making it more efficient and coating chemically pure manganese layer. Because the CSMM membranes are inherently cation-selective, meaning H^+ ions would also pass through, making HER still an obstacle. By chemically functionalizing carbon nanotube membranes [8,9], even greater selectivity can be achieved, effectively mitigating the HER. Although these advanced membranes show promising potential, they remain difficult to implement, and research about their implementation in electrochemical deposition is scarce; in the majority of cases, to make electrodeposition more efficient, additives to the electrolyte are used, making them the most common and practical approach to enhancing electrodeposition efficiency.

Without additives, manganese electrodeposition yields very poor results, even under optimal electrolyte concentration, pH value, or high current density [10]. Group VI elements, such as sulfur, selenium, and tellurium, additives are viewed as essential because they alter the overvoltage of the water reduction reaction differently [4]: SO_2 has the lowest effect, SeO_2 compounds have a moderate effect, and TeO_2 has the strongest effect. As the water reduction reaction is suppressed, to an extent, electrodeposition in this instance is favored, and, in turn, the effectiveness of the deposition increases. In acid aqueous electrodeposition, Te can adsorb onto active deposition sites within the Mn lattices in active deposition sites [11,12]. Hydrogen gets effectively repelled by tellurium from the coating's surface, mitigating HER and making it less predominant. As Te blocks incoming manganese ions, it prevents the formation of crystal planes. This creates internal stress and lattice distortion within the Mn deposit. For example, α -Mn cubic crystals become small in size due to introduced stress and lattice distortion within the Mn coating. This mechanism serves as a pathway to preferentially deposit a fine-grained α -Mn phase, ultimately producing a denser and harder coating. However, it should be noted that an increased MASB temperature during the deposition will naturally cause the α -Mn phase to dominate the coating surface.

The dissolution of sodium tellurate is important to prevent the formation of MnTe compounds, especially at the beginning of the electrodeposition when the tellurium concentration is highest. It was observed that if sodium tellurate is not thoroughly or not

sufficiently dissolved beforehand, the MASB electrolyte becomes cloudy. It is suspected that compounds such as MnTeO_4 form, which show very low solubility in water. For that reason, tellurium(IV) oxide would fail to form, and elemental tellurium would not be present to assist the electrodeposition process by suppressing HER. Consequently, orthotelluric acid is unsuitable to be used on its own without prior treatment (dissolution), as it was discovered in other research [13]. Tellurium compounds [14] such as tellurous acid or metatelluric acid could be potential candidates to serve as sodium tellurate alternatives, but they are poorly characterized, and relevant research is limited. Hydrogen telluride was considered as an alternative, but it is highly unstable and readily decomposes into water and elemental tellurium (in the presence of air and oxygen); it also has poor solubility in water. Nevertheless, if dissolved, it could react within the electrolyte solution, forming insoluble MnTe compounds with Mn^{2+} ions. Based on a comprehensive literature review, there seems to be no other viable compound currently discovered to be used instead of Na_2TeO_4 . This conclusion is supported by the theoretical analysis presented in this work.

In the industrial setting, SO_2 is widely used due to the possibility of obtaining high-purity manganese coatings at the expense of non-ideal coating morphology [15] and lower current efficiency [16]. Conversely, selenium compounds are toxic [17] and deposit coatings of lower chemical purity, although they offer the advantage of controlling the morphology of the deposited coating [18,19].

As previously noted, research on tellurium additives and how they improve manganese electrodeposition is scarce. Nonetheless, existing literature indicates that even trace amounts of tellurium compounds can improve current efficiency [20,21]. Furthermore, tellurium is lower in its toxicity to the environment than selenium compounds [22].

Despite the distinct limitations, additives are still being used and new additives are being tested and developed to further improve electrodeposition efficiency. Recent investigations into new organic and inorganic additives show promising results [23,24], with a primary focus on minimizing structural impurities within the resulting coatings.

The chosen substrate, ASTM A283 Grade A steel plate is often utilized for the manufacturing of structural and framework components, construction, storage tanks and many more [25,26]. This versatility and wide variety of uses make this substrate an adequate candidate for electrodeposition and anticorrosion testing. Standard metal sheet production methods of steel (hot-rolling or cold-rolling) and pickling typically produce the substrate's surface roughness between 6.3 and 12.5 μm (if pickled, i.e., acid washed, the surface can become smoother: 3–6 μm) [25,27]. While hot-rolling and cold-rolling techniques provide distinct mechanical advantages, the critical step is tempering or annealing temperatures. The annealing-rolling process can increase grain size and improve elongation [28], whereas optimal tempering temperature can increase impact toughness [29]. Recently, novel experiments have focused on mitigating issues associated with excessive substrate surface roughness [30]. While it is preferred that there be a certain degree of microscopic texture to promote coating adhesion, extreme surface roughness could be a hinderance; for example, during electrodeposition metal ions would preferentially deposit on high points, peaks, which leads to uneven deposition.

Based on previous studies [31,32] a cathodic current density of 15 A/dm^2 within the given temperature range from 20 $^{\circ}\text{C}$ to 80 $^{\circ}\text{C}$, these parameters offer the potential to achieve optimal quality in electrodeposited manganese coatings under these specific conditions while effectively revealing temperature-dependent physical or chemical alterations. It was chosen that electrodeposition will last for 7 min, meaning that the metal plate will receive an electric charge of 504 $\text{A}\cdot\text{s}$ (coulombs). As other studies concluded, current efficiency leading up to around 10 min sharply peaks, and beyond this point begins to steadily decline [33,34], i.e., coating thickness increases with faltering current efficiency

as time progresses. By looking at previously done studies and basing current efficiency on deposition time, the thickness of the coating could be somewhat approximated. By correlating current efficiency with deposition time based on historical data, the coating thickness can be reasonably approximated. For instance, it was demonstrated that an 8 min deposition time coupled with a temperature increase from 20 °C to 80 °C exhibited a slight exponential dependence on current efficiency, rising from 37% to 71%, respectively [35]. This means that by knowing the theoretical mass of the electrodeposited coating, the lasting deposition time, current efficiency and theoretical approximation of coating thickness could be calculated by applying Faraday's law [36]:

$$m_t = \frac{A_{Mn} \cdot I \cdot t}{Z_{Mn} \cdot F}; \eta = \frac{\Delta m}{m_t} (\cdot 100\%); \quad (1)$$

$$V = \frac{\Delta m}{\rho_{Mn}} \Rightarrow \Delta m = a_{th} \cdot \rho_{Mn} \cdot P; \quad (2)$$

$$\eta = \frac{a_{th} \cdot \rho_{Mn} \cdot P \cdot Z_{Mn} \cdot F}{A_{Mn} \cdot I \cdot t} \Rightarrow a_{th} = \frac{A_{Mn} \cdot I \cdot t \cdot \eta}{\rho_{Mn} \cdot P \cdot Z_{Mn} \cdot F} \quad (3)$$

where η —current efficiency; A_{Mn} —metal atomic mass, g/mol; I —current intensity, A; t —deposition time, s; Z_{Mn} —metal charge, units; F —Faraday constant, C/mol; ρ_{Mn} —manganese density g/cm³; P —effective plate surface area, cm²; a_{th} —coating thickness, cm; Δm —mass change in the substrate, before and after the deposition, that is interpreted as coating mass, g; m_t —theoretical coating mass, g; V —volume, cm³.

These predictive calculations (Table 1) serve as a valuable tool when a specific coating thickness is required across various applications, provided the current efficiency is acceptable, i.e., if the process efficiency is justified in large-scale production of manganese coatings.

Table 1. Theoretical Mn coating thickness based on calculations derived from theoretical current efficiency and an 8 min deposition time.

Electrolyte Temperature During Electrochemical Manganese Deposition, °C	Theoretical Current Efficiency, %	Theoretical Coating Thickness, µm
20	37	10.2
40	42	11.5
60	53	14.5
80	71	19.5

Manganese coatings on their own are rarely utilized for the sole purpose of anticorrosion; when applied, their primary function is as a cathodic sacrificial layer for steel [37], creating a protective manganese hydroxide layer. Because manganese is inherently brittle it is often used in creating alloys, which are superior; although manganese alloys have been proven to have higher corrosion resistance their performance remains inferior compared to that of phosphated manganese coatings [38]. Phosphating is an effective method to enhance coatings corrosion resistance [39]. These treatments are classified as conversion coatings because they chemically transform the metal surface into a rough, amorphous, or crystalline phosphate composite layer. Previous research has demonstrated that zinc phosphating processes show significant promise due to their high anticorrosion capabilities [40]. These coatings provide superior adhesion and high corrosion resistance as compared to untreated surfaces that had not undergone such a process.

This study aims to investigate the influence of manganese ammonium sulfate bath (electrolyte) temperature, coupled with the addition of a tellurium(VI) compound, on the substrate surface morphology and electrodeposition efficiency, as well as to evaluate the

anticorrosion properties of the resulting phosphated manganese coatings. Furthermore, theoretical predictions based on previous studies were taken into account and mathematical predictions which are based on them will be tested. Ultimately, the primary objective is to determine the optimal electrochemical parameters for producing high-quality deposits and compare corrosion results with untreated steel plates.

2. Materials and Methods

All chemicals used in this study were of analytical grade (Eurochemicals, Vilnius, Lithuania), and for the preparation of all solutions, twice-distilled water with resistivity $\geq 5 \text{ M}\Omega\cdot\text{cm}$ was used. To separate cathodic and anodic compartments, a thermally treated PVC membrane meshed onto a PVC carcass was used. The MASB temperature was monitored using a Lab Box Pt1000 (Lab Box, Premià de Dalt, Spain) temperature sensor that was connected to a magnetic stirrer. Current strength was regulated by a power source (Matrix MPS-30005S DC power supply (Matrix Technology Inc., Shenzhen, China)), and an ammeter (Mastech MS8268 (Mastech Group, Shenzhen, China)) was used to ensure an even distribution of current.

2.1. Electrodeposition

Manganese coatings for corrosion tests were electrodeposited on mild carbon steel (ASTM A283, grade A) that has 0.08 dm^2 of active surface area (2 cm by 2 cm on both sides of the plate); a 2–3 cm extension was maintained for holding the plate during the experiments. Prior to electrodeposition, the substrates were cleaned before electrodeposition by immersion in a 10% NaOH solution for degreasing, then washing them with twice-distilled water, then etching them with a 5% HCl solution, and washing them again with twice-distilled water. Electrodeposition was performed in an ammonium manganese sulfate electrolyte bath that consisted of 0.62 mol/L $\text{MnSO}_4\cdot 5\text{H}_2\text{O}$; 0.95 mol/L $(\text{NH}_4)_2\text{SO}_4$ and 0.22 mmol/L $\text{Na}_2\text{TeO}_4\cdot 2\text{H}_2\text{O}$ (pH was maintained at around ~ 2.33 with a 10% H_2SO_4 solution). The pH levels were kept acidic for sodium tellurate solubility. In the MASB bath, which consists of twice-distilled water, the solubility of $\text{Na}_2\text{TeO}_4\cdot 2\text{H}_2\text{O}$ is 0.8 g/100 g when the temperature is 25°C [41]. But with the addition of sulfuric acid, sodium tellurate is turned into orthotelluric acid, H_6TeO_6 (also shown as $\text{Te}(\text{OH})_6$), which has much greater solubility in water (up to 50.1 g/100 g of water at 30°C) [42].

2.2. Electrochemical Tests

Short-term electrochemical studies of the corrosion of manganese coatings were performed at room temperature ($21 \pm 1^\circ\text{C}$). The three-electrode electrochemical cell was composed of a naturally aerated 3% NaCl aqueous solution, a Pt wire (surface area of $\sim 15 \text{ cm}^2$) was used as a counter electrode, and Ag/AgCl sat. $\text{KCl}_{(\text{aq})}$ was used as a reference electrode (all potentials in this work are provided with respect to this specific saturated electrode). The distance between the three electrodes was kept at $\sim 4 \text{ cm}$. The raw steel extensions of the electrodeposited plates were isolated using an epoxy resin coating to ensure that only the manganese-coated surface area was evaluated. Corrosion potential and potentiodynamic polarization curves were recorded using a BioLogic SP-150 potentiostat-galvanostat (BioLogic, Seyssinet-Pariset, France) interfaced with EC-Lab v10.39 software (BioLogic, Seyssinet-Pariset, France). Using the Tafel approximation of the Butler–Volmer equation and by extrapolation of the recorded potentiodynamic polarization curves with the Tafel fit curve, corrosion parameters, such as the equilibrium corrosion potential and corrosion current density, were calculated using the EC-Lab v10.39 software.

Long-term electrochemical studies of the corrosion of manganese coatings were performed at room temperature ($21 \pm 1^\circ\text{C}$). The open circuit voltage (OCV) or corrosion

potential of coatings was measured using a two-electrode system: the test electrode was a phosphated manganese-coated steel substrate, and the reference electrode was a silver–silver chloride electrode filled with saturated KCl solution. The test medium was a naturally aerated 3% NaCl aqueous solution. The variation in OCV over time was registered by using a data logger PicoLog TC-08 (Pico Technology Limited, St Neots, United Kingdom) connected via USB to a personal computer and monitored with PicoLog software v.6.2.11 (Pico Technology Limited, St Neots, United Kingdom).

2.3. Phosphate Treatment

Manganese coating corrosion resistance was improved by phosphating in a solution, which was as follows: 0.34 mol/L H_3PO_4 , 0.17 mol/L $\text{Zn}(\text{NO}_3)_2$, 0.4 mol/L NaNO_3 (pH was controlled and maintained at ~ 2.35 with 2 M NaOH solution). Phosphating was performed at room temperature ($21 \pm 1^\circ\text{C}$) for 20 min [43,44].

2.4. Structural, Elemental and Morphological Analysis

Scanning electron microscope (SEM) pictures were taken by a S 3400N (Hitachi, Hitachinaka, Japan); settings were as follows: low vacuum setting, electron accelerating voltage 5–15 kV, working distance 7.5–10 mm, LFD detector.

Energy-dispersive X-ray spectroscopy (EDX) data were collected using the previously mentioned SEM apparatus with a spectrometer Xflash QUAD 5040 (Bruker, Berlin, Germany); settings were as follows: low vacuum setting, electron accelerating voltage 15 kV, working distance 9.9–10.1 mm, SDD detector.

X-ray diffraction (XRD) analysis of corrosion products formed on the surface of Mn coatings was performed using an X-ray diffractometer D8 DISCOVER (Bruker, Karlsruhe, Germany). Data were analyzed by PDF-2 (International Centre for Diffraction Data (ICDD), Newtown Square, PA, USA).

3. Results

3.1. The Effect of Temperature on the Thickness and Current Efficiency of Electrodeposited Manganese Coatings

After performing electrochemical deposition of manganese coating at selected temperatures, the current efficiency and deviations were calculated (Figure 1 and Table 2). The results demonstrate a direct correlation between operating conditions and process performance: higher electrolyte temperatures yield significantly increased current efficiency.

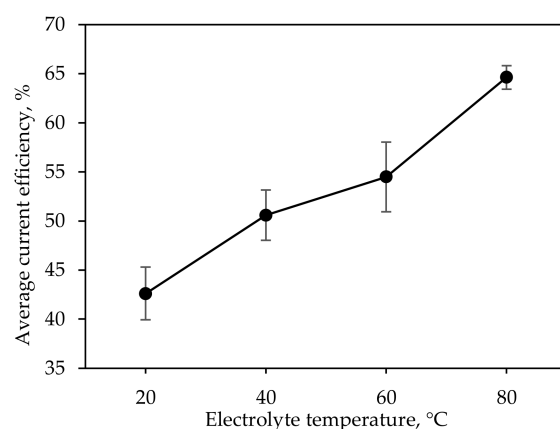
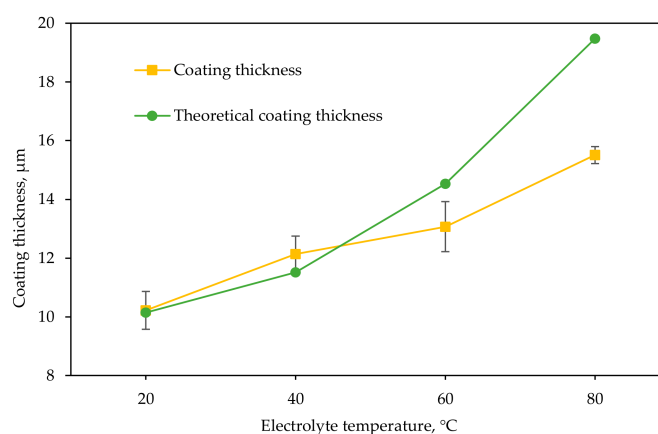


Figure 1. Influence of temperature on the current efficiency of coatings from MASB when the deposition time is 7 min.

Table 2. Influence of temperature on average current efficiency from MASB when the deposition time is 7 min.

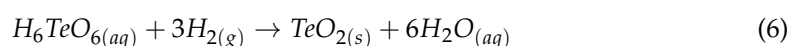
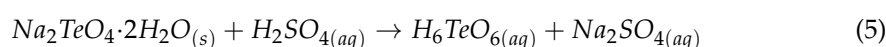
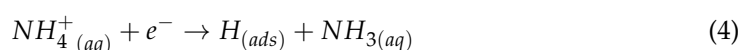
Electrolyte Temperature During Electrochemical Manganese Deposition, °C	Average Current Efficiency, %	Average Current Efficiency Deviation, %
20	42.6	2.7
40	50.6	2.6
60	54.5	3.6
80	64.6	1.2

Furthermore, elevated temperatures were directly associated with increased coating thickness (from 10.22 μm to 15.51 μm respectively), indicating that a greater amount of material was deposited on the substrate. At lower temperatures, these values closely align with the theoretical coating thickness theoretical calculations derived from Faraday's law equations. However, as the electrolyte temperature increases, the theoretical thickness begins to outpace the experimentally observed values (Figure 2).

**Figure 2.** Direct comparison of Mn coating thicknesses between experimental deposition and theoretical calculations and how they are influenced by the temperature of MASB.

3.2. Effect of Temperature on the Composition of Electrolytic Mn Coatings

EDS analysis demonstrates that an increase in electrolyte temperature directly correlates with an elevated concentration of tellurium within the manganese coating (Figure 3). The amount of oxygen in the coating remains the same throughout all electrolyte temperatures (2.5 ± 0.5 wt.%). The higher tellurium content obtained at elevated deposition temperatures and high current density can be attributed to the formation of mono- and ditelluride variants (MnTe (hexagonal phase), MnTe_2 (cubic phase), or traces of elemental Te) at high deposition temperatures combined with high current density [21] or by the higher solubility of H_6TeO_6 . Because atomic hydrogen is generated from the electrochemical discharge during the decomposition of the ammonium sulfate, reduction in orthotelluric acid proceeds as follows [21]:



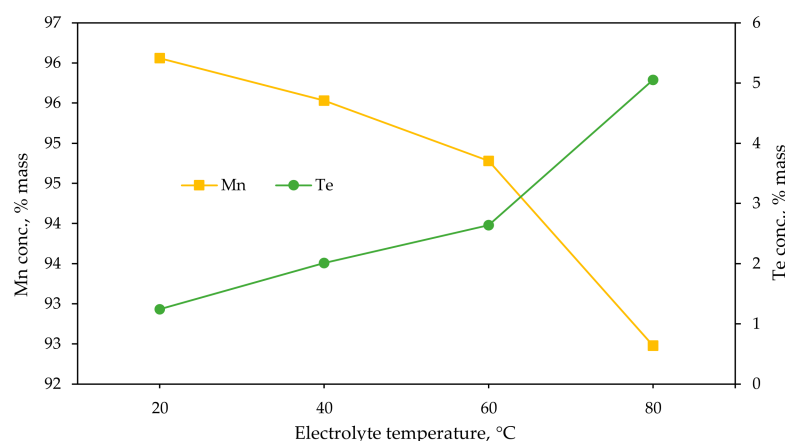
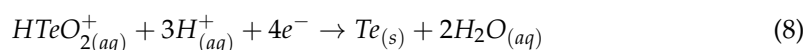
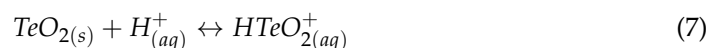


Figure 3. Influence of MASB temperature on Te and Mn concentrations (% mass) in deposited Mn coatings.

Because of baths acidity TeO_2 form HteO_2^+ cations which can be reduced electrochemically to elemental Te [21]:



Although EDS analysis confirmed the presence of trace tellurium, it remained undetectable via XRD analysis. As the temperature of the electrolyte increased (Figure 4), so did the amount of α -Mn (PDF 04-007 5288) as is expected [45]. Minor, unconfirmed peaks of β -Mn (PDF 03-065-9738) and γ -Mn (PDF 00-017-0910) allotropes were noticed in the diffractograms, but their presence may be attributed to the highly disordered or amorphous nature of the material deposited at lower temperatures and high current density. Furthermore, the phase transformation of metastable β -Mn and γ -Mn requires a prolonged duration and higher temperatures to transform into the thermodynamically stable α -Mn [45].

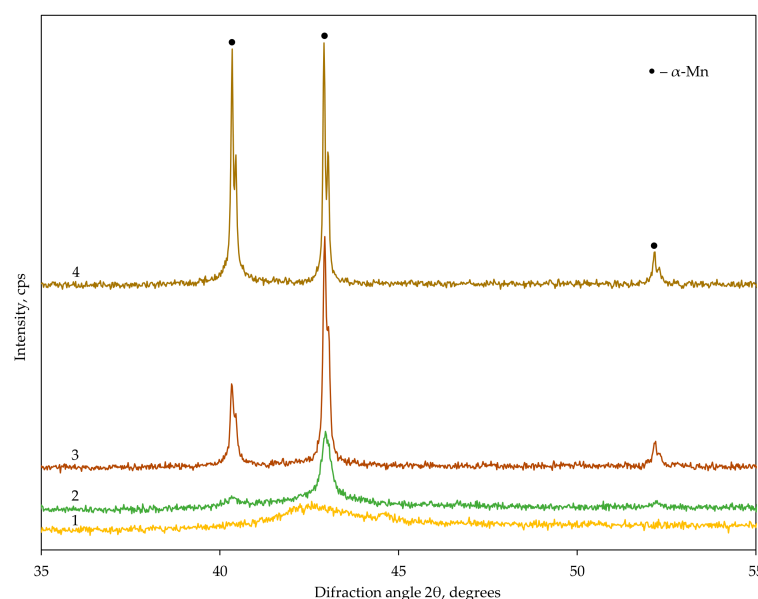


Figure 4. XRD patterns of Mn coatings deposited from MASB at temperatures of: (1) 20 °C; (2) 40 °C; (3) 60 °C; (4) 80 °C.

3.3. The Influence of Temperature on the Structure and Morphology of Electrolytic Mn Coatings

As shown in Figure 4, the α -Mn phase becomes increasingly prevalent as the electrolyte temperature rises; this phase development can be observed in the coating's surface morphology where the α -Mn phase is seen as distinct cubic crystals (Figure 5h).

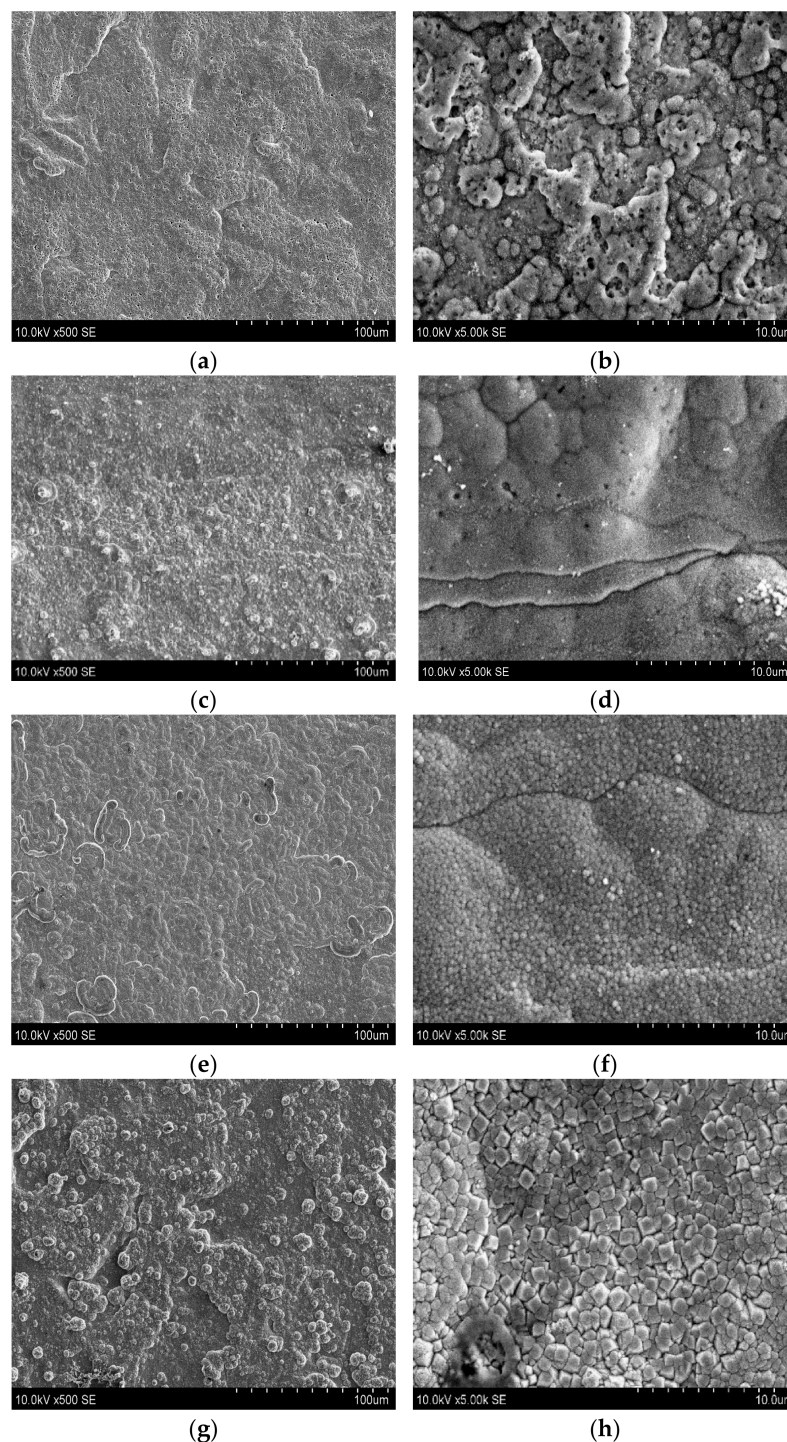


Figure 5. SEM images at different magnifications of the surface of Mn coatings deposited at various electrolyte temperatures: (a,b) 20 °C; (c,d) 40 °C; (e,f) 60 °C; (g,h) 80 °C, general view magnification (a,c,e,g)— $\times 500$ and close-up (b,d,f,h)— $\times 5000$.

A comparison of the images in Figure 5b,d,f,h shows that α -Mn gains pore prevalence and is more noticeable due to its cubic structure. As stated before, β -Mn and γ -Mn take time

and higher temperatures to transform into α -Mn. Images a-d show coatings on an amorphous surface that has not transformed to the α -Mn phase at low deposition temperatures.

3.4. Phosphated Manganese Coatings' Composition and Morphology

As shown in Figure 6, phosphated manganese coatings generate various crystalline compounds, although $\text{Zn}_3(\text{PO}_4)_2(\text{H}_2\text{O})_4$ and $\text{Zn}_4(\text{PO}_4)_2(\text{OH})_2(\text{H}_2\text{O})_3$ are most prominent [44]. In the diffraction angle range 40–45 2θ , the same amorphous manganese and α -Mn can be viewed as in Figure 6. This suggests that the various metal phosphate compounds generated during the phosphating process do not completely cover the underlying manganese coating surface. Identified compounds were: α -Mn (PDF 04-002-1283), $\text{Zn}_3(\text{PO}_4)_2(\text{H}_2\text{O})_4$ (PDF 04-010-4349), $\text{Zn}_4(\text{PO}_4)_2(\text{OH})_2(\text{H}_2\text{O})_3$ (PDF 04-012-5397), $\text{Zn}_4(\text{SO}_4)(\text{OH})_6(\text{H}_2\text{O})_3$ (PDF 01-082-3605), $\text{Zn}_{2.5}\text{Mn}_{0.5}(\text{PO}_4)_2(\text{H}_2\text{O})_4$ (PDF 04-023-0786); $\text{Mn}_2\text{Zn}(\text{PO}_4)_2(\text{H}_2\text{O})_4$ (PDF 00-065-0457); NH_4ZnPO_4 (PDF 00-022-1048).

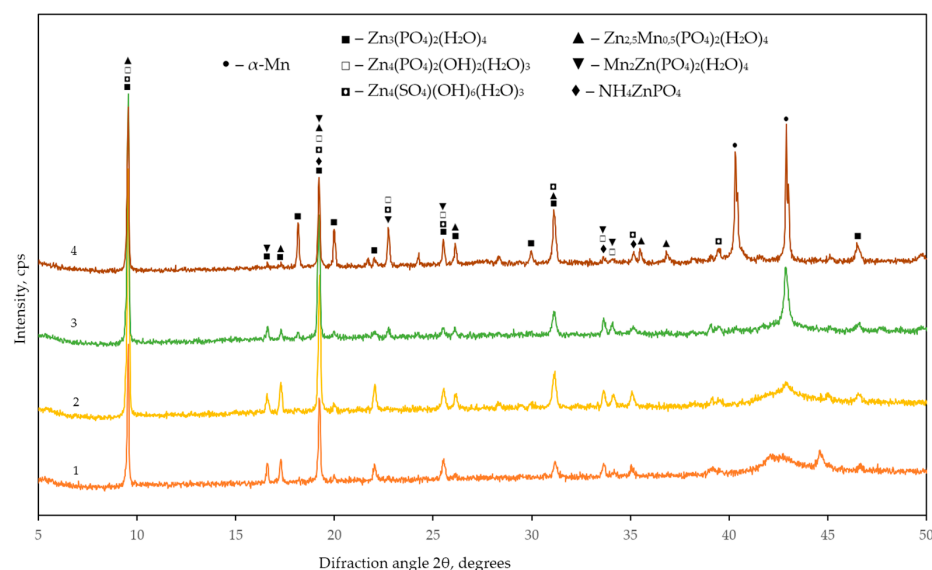


Figure 6. XRD patterns of phosphated manganese coatings at room temperature at different MASP temperatures: (1) 20 °C; (2) 40 °C; (3) 60 °C; (4) 80 °C.

As the analysis of Figure 6 showed, the EDS analysis and SEM images of the surface chemical composition of phosphated manganese coatings show that not all of the surface is covered by metal phosphate crystals (Table 3 and Figure 7).

Table 3. EDS analysis of the chemical composition of Figure 7.

Element	C	Zn	Mn	P	O	Fe	Te	K
(a), % mass	0.81	46.50	4.49	16.22	30.68	1.24	0	0
(b), % mass	0.70	26.95	31.64	14.19	19.32	1.22	4.28	1.70

The morphology of the newly formed crystals (Figure 7a) and the affected manganese surface (Figure 7b) differ in chemical composition (Table 3). This shows that the crystals are composed of zinc phosphate compounds. The morphology of the seemingly cracked spheres consists of manganese and phosphorus compounds or manganese-zinc phosphates. Observed microcracks can be attributed to the evolution and release of hydrogen gas, a process known to induce coating damage [46], which occurs as a byproduct during the synthesis of metal phosphate conversion layers.

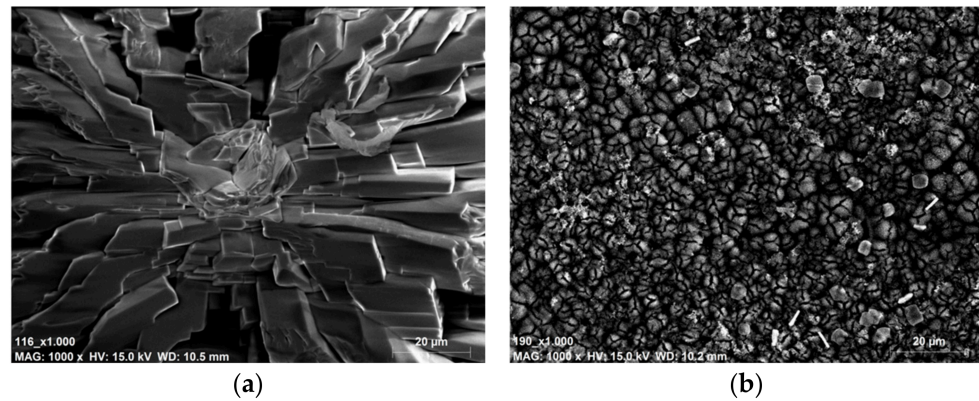


Figure 7. SEM images of at-room-temperature phosphated manganese coatings, when MASB temperature is 80 °C, in various locations, magnification: (a,b)— $\times 1000$.

The unexplained small traces of potassium shown in Table 3 can be explained by: peak overlaps that lead to false positives, automatic EDS system identification of an element, and cross-contamination between samples. Elemental mapping of phosphated manganese coatings shows elemental dispersion within the coating (Figure 8).

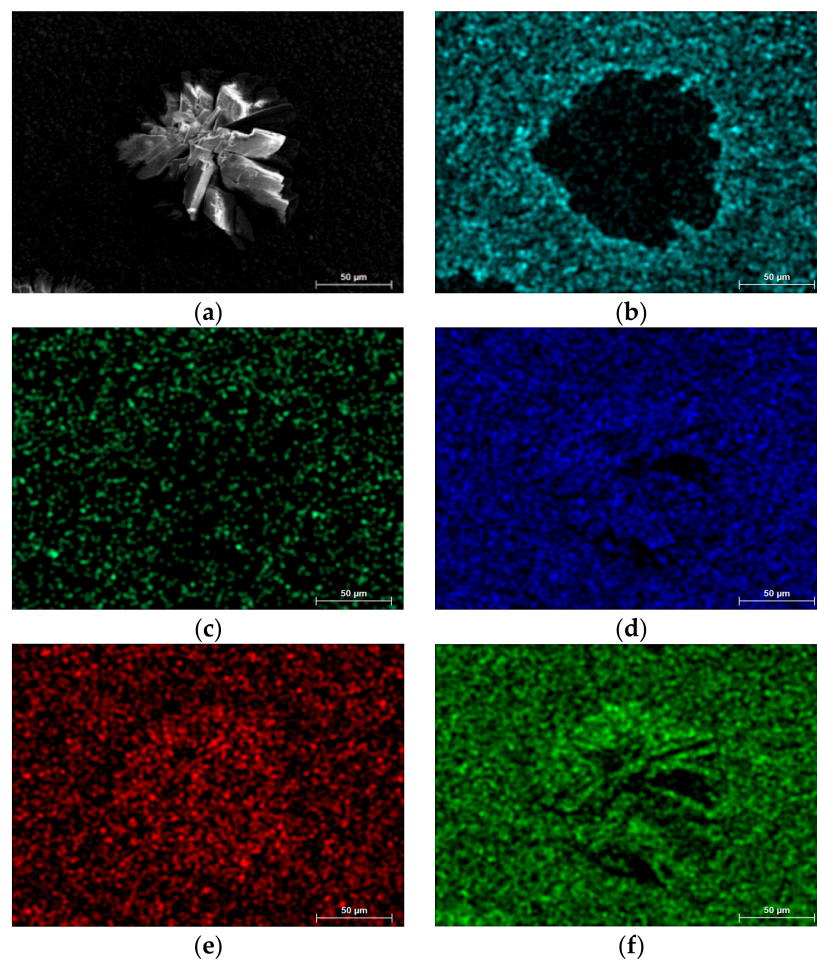


Figure 8. EDS elemental mapping of manganese coatings phosphated at room temperature and deposited at 80 °C MASB, magnification $\times 3000$, displaying pictures of elements: (a) SEM picture; (b) Mn; (c) Te; (d) P; (e) Zn; (f) O.

The morphology observed in Figure 7b corroborates the findings presented in Figure 8 and Table 3, confirming that the newly formed crystals primarily consist of zinc-based and manganese-based metal phosphates and sulfates.

3.5. Phosphated Manganese Coatings' Long-Term and Short-Term Corrosion Results in 3% NaCl Solution

Potentiodynamic polarization analysis reveals a decrease in the anodic Tafel slope coating values for all phosphated manganese coatings (Figure 9), which means that the overall corrosion process is predominantly controlled and inhibited by the cathodic reaction kinetics.

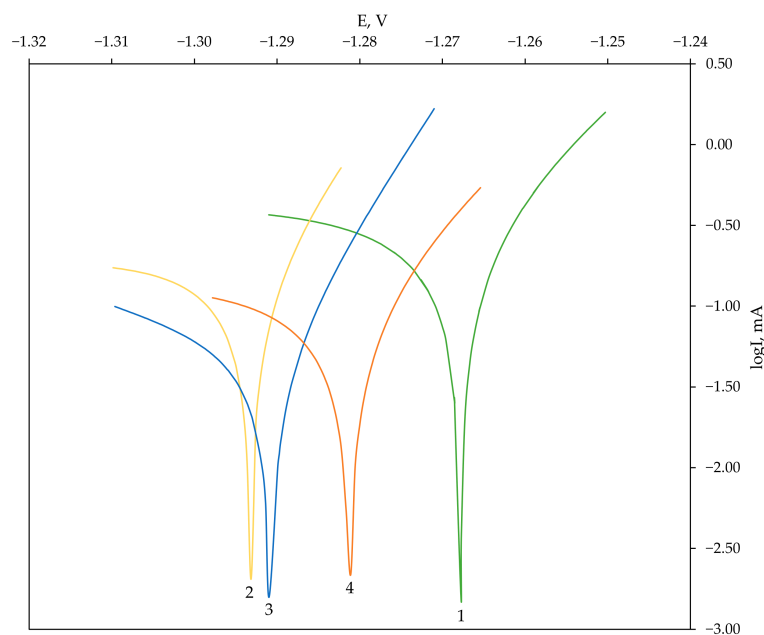


Figure 9. Potentiodynamic polarization curves of manganese coatings phosphated at room temperature and deposited at different MASB temperatures: (1) 20 °C; (2) 40 °C; (3) 60 °C; (4) 80 °C.

Tafel extrapolation was utilized to determine the anodic (β_a) and cathodic (β_c) Tafel constants, the corrosion potential (E_{corr} , representing the thermodynamic tendency to corrode), and the corrosion current density (I_{corr} , representing the kinetic corrosion rate); the corrosion rate was calculated by extrapolating Tafel corrosion calculations as shown in Table 4. The lowest corrosion rate was observed for the phosphated manganese coating electrodeposited from the MASB at 60 °C. Overall, a clear trend emerges showing that the corrosion rate decreases as the MASB deposition temperature increases, whereas the corrosion potential remains relatively constant across all investigated temperatures. The short-term corrosion rates calculated for these coatings confirm that this trend of enhanced corrosion resistance persists. The initial kinetic data were used to estimate coating longevity; a projection of the service life can be speculated: corrosion of millimeters per year (Table 4).

Table 4. Corrosion characteristics of manganese coatings phosphated at room temperature and deposited at different MASB temperatures in naturally aerated 3% NaCl solution.

Electrolyte Temperature, °C	E_{corr} , mV (Ag/AgCl)	CR, mmpy	I_{corr} , $\mu\text{A}/\text{cm}^2$	β_a , mV/Dec	β_c , mV/Dec
20	−1268	0.179	119.1	15.1	37.7
40	−1293	0.105	69.7	10.6	36.2
60	−1291	0.073	48.9	12.9	59.7
80	−1281	0.079	52.9	15.3	48.2

For comparison, ASTM A283 steel substrate, neither coated with manganese nor phosphate, was examined as a control sample. It was observed that although the initial corrosion rate appeared low, this uncoated substrate still exhibited susceptibility to accelerated corrosion over time (Table 5), although it is acknowledged that the coating is a temporary shield preventing steel corrosion; while the phosphate Mn coating deposited at various MASB temperatures is actively corroding and dissolving, it is physically blocking the steel underneath from oxidizing. This comparison demonstrates the primary utility of the phosphated manganese coatings: they are effective when deployed as sacrificial coatings for protection against corrosion.

Table 5. ASTM A283 steel plate corrosion characteristics.

E_{corr} , mV (Ag/AgCl)	I_{corr} , $\mu\text{A}/\text{cm}^2$	β_a , mV/Dec	β_c , mV/Dec
−683	17.0	23.3	23.0

Long-term corrosion tests (Figure 10) show that the phosphated manganese coating deposited at an MASB temperature of 20 °C experiences a rapid degradation of its corrosion potential within the first 6 h of immersion, subsequently stabilizing at −900 mV. A similar but less pronounced degradation trend is observed for the coating deposited at 40 °C; however, its potential stabilizes much more rapidly and stabilizes at −1175 mV. Coatings deposited at 60 °C and 80 °C MASB temperature maintain electrochemical stability, maintaining a stable corrosion potential during the first 12 h.

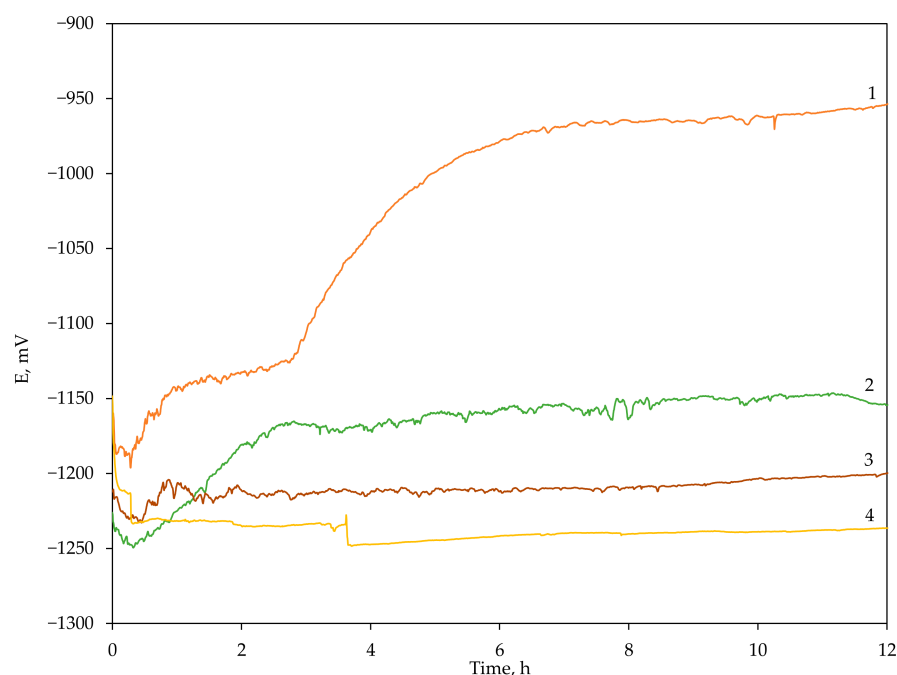


Figure 10. Change in free corrosion potential over time (12 h) of phosphated at room temperature manganese coatings obtained at different MASB temperatures: (1) 20 °C; (2) 40 °C; (3) 60 °C; (4) 80 °C.

Due to the rapid loss of corrosion potential for the phosphated manganese coating deposited at an electrolyte temperature of 20 °C, its data were omitted from Figure 11 to avoid redundancy. Similar electrochemical trends persist when the exposure period is extended to 48 h. The phosphated coating electrodeposited at 80 °C exhibits the most stable corrosion potential over the 48 h testing duration. The corrosion potential remains relatively unchanged between −1220 mV and −1250 mV for the first 20 h. However, after 20 h, it can be observed that the corrosion potential begins to steadily rise to −1200 mV. For the

phosphated coating deposited at 60 °C MASB, the open-circuit potential increases steadily over a 34 h period, moving from −1220 mV to −1130 mV. At this point, the coating's free corrosion potential stabilizes and remains unchanged until 48 h. In contrast, for the phosphated coating deposited at 40 °C MASB the change in corrosion potential occurs during the first 15 h from −1250 mV to −1140 mV and then stabilizes. Interestingly, the upward trend in corrosion potential for the phosphated coating deposited at 80 °C MASB coating appears to continue progressively even past the 48 h mark.

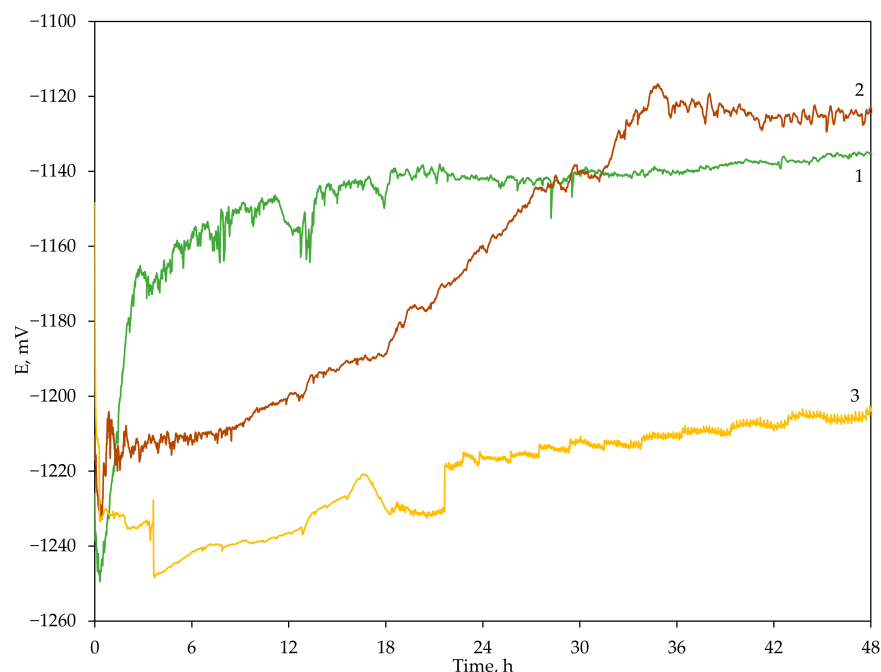


Figure 11. Change in free corrosion potential over time (48 h) of phosphated at room temperature manganese coatings at different MASB temperatures: (1) 40 °C; (2) 60 °C; (3) 80 °C.

4. Conclusions

Previous studies have demonstrated that Te(VI) additives significantly enhance the current efficiency of manganese electrodeposition by suppressing the competing hydrogen evolution reaction (HER) at the cathode surface and directly modifying the manganese crystal structure. The influence of Te(VI) additives combined with high MASB temperature and high current density of 15 A/dm² (receiving an electric charge of 504 A·s (coulombs)) produces a stable α -Mn coating that could be further improved by the phosphating process.

This study tries to make mathematical predictions that were derived from previous works in the field in predicting coating thickness provided the same or similar efficiency. At lower deposition temperatures (from 20 °C to 40 °C), the experimental data align well with the theoretical predictions. However, as the electrolyte temperature increases (from 60 °C to 80 °C), the experimental results begin to deviate significantly from the calculated values, indicating a breakdown in the predictive capacity of the model at elevated temperatures.

As the MASB electrolyte temperature increases, the surface concentrations of tellurium and manganese begin to diverge; Te increases, and Mn decreases. Literature analysis suggests that this phenomenon can be attributed to the thermally activated formation of MnTe compounds at higher temperatures and the increased solubility of sodium tellurate and orthotelluric acid, thereby increasing the mass transport and subsequent incorporation of tellurium into the electrodeposited coating.

High current yield and the highest thickness of the Mn coating were achieved at the highest deposition temperatures (the difference in efficiency between electrolyte tempera-

tures of 20 °C and 80 °C is around 22%; the difference in average coating thickness between electrolyte temperatures of 20 °C and 80 °C, at deposition is 4.8 µm).

The utility of these sacrificial phosphated manganese coatings is evaluated primarily on the basis of their inherent degradation rates. By utilizing the initial corrosion rates to estimate coating longevity, a clear projection of the service life can be established. Based on these initial kinetic data, the estimated lifespan of the coatings scales progressively with the MASB deposition temperature: phosphated Mn coating deposited at 20 °C MASB temperature could last up to 21 days, phosphated Mn coating deposited at 40 °C MASB temperature could last up to 42 days, phosphated Mn coating deposited at 60 °C MASB temperature could last up to 65 days, and phosphated Mn coating deposited at 80 °C MASB temperature could last up to 72 days.

The temperature of electrochemical deposition alters the coating surface, i.e., α -Mn produces a surface of rough characteristics; it does not significantly affect the increase in the mass of coatings after the phosphating process. On average, the coatings become 0.0044 g (0.55 mg/cm²) heavier. This uniform accumulation suggests that substrate surface morphology does not play a critical role in determining phosphating efficiency.

Electrochemical evaluations demonstrate that phosphated manganese coatings deposited at higher electrolyte temperatures exhibit lower corrosion rates. 12 h and 48 h corrosion tests show that phosphate coatings deposited at higher MASB temperatures maintain a more stable corrosion potential that takes longer to reach. Free corrosion potential of phosphated Mn coating deposited at 20 °C MASB stabilizes after 6 h; phosphated Mn coating deposited at 80 °C MASB does not stabilize even after 48 h.

Author Contributions: Conceptualization, V.S.; Methodology, V.S., E.G. and N.Ž.; Software, E.G.; Validation, E.G. and N.Ž.; Formal analysis, V.S.; Investigation, V.S.; Resources, V.S., E.G. and N.Ž.; Data curation, V.S., E.G. and N.Ž.; Writing—original draft, V.S.; Writing—review & editing, V.S., E.G. and N.Ž.; Visualization, V.S.; Supervision, E.G. and N.Ž.; Project administration, N.Ž. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Global Manganese Market. Available online: https://www.researchgate.net/publication/385565279_GLOBAL_MANGANESE_MARKET (accessed on 13 April 2025).
2. Behera, A.; Patel, P.; Ghosh, A.; Tripathy, A.; Sahoo, S.K. Pyrometallurgical processing of manganese ore. *Eng. Res. Express* **2024**, *6*, 035010. [CrossRef]
3. Zhang, K.; Liu, Z.; Qiu, X.; Rao, S.; Zhu, W. Hydrometallurgical recovery of manganese, gold and silver from refractory Au-Ag ore by two-stage reductive acid and cyanidation leaching. *Hydrometallurgy* **2020**, *196*, 105406. [CrossRef]
4. Lu, J.; Dreisinger, D.; Glück, T. Manganese electrodeposition-A literature review. *Hydrometallurgy* **2014**, *141*, 105–116. [CrossRef]
5. Lewis, J.E.; Scaife, P.H.; Swinkels, D.A.J. Electrolytic manganese metal from chloride electrolytes. I. Study of deposition conditions. *J. Appl. Electrochem.* **1976**, *6*, 199–209. [CrossRef]
6. Wang, Z.; Zhang, Y.; Yang, B.; Li, W.; Zhu, H.; Zeng, X.; Liu, S. The road ahead for hydrogel electrolytes in aqueous zinc metal batteries. *Iontronics* **2026**, *2*, 16. [CrossRef]
7. Luo, C.; Zhou, L.; Xu, R.; Hou, Y.; Hou, X. CNT array-based aluminum bipolar electrode iontronic memristors. *Iontronics* **2026**, *2*, 6. [CrossRef]
8. Wang, R.; Chen, D.; Wang, Q.; Ying, Y.; Gao, W.; Xie, L. Recent advances in applications of carbon nanotubes for desalination: A review. *Nanomaterials* **2020**, *10*, 1203. [CrossRef] [PubMed]

9. Yang, G.; Xie, Z.; Zhang, S.; Zheng, H.; Cai, K.; Cran, M.; Ng, D.; Wu, C.; Gray, S. Functionalized carbon nanotube-mediated transport in membranes containing fixed-site carriers for fast pervaporation desalination. *ACS Appl. Mater. Interfaces* **2020**, *12*, 50918–50928. [CrossRef] [PubMed]
10. Paiva, A.P.; Li, Y.; Pan, X.; Horri, B.A. Advancements in sustainable electrolytic manganese recovery: Techniques, mechanisms, and future trends. *Recycling* **2025**, *10*, 26. [CrossRef]
11. Tao, H.; Sun, X.; Back, S.; Han, Z.; Zhu, Q.; Robertson, A.W.; Ma, T.; Fan, Q.; Han, B.; Jung, Y.; et al. Doping palladium with tellurium for the highly selective electrocatalytic reduction of aqueous CO₂ to CO. *Chem. Sci.* **2018**, *9*, 483–487. [CrossRef] [PubMed]
12. Tang, X.; Zhang, Y.; Tao, T.; Zhang, B.; Du, M.; Tu, M.; Liang, S.; Han, J.; Tang, W.; Gong, J. Versatile roles of modifiers in crystal growth and morphology modification of lithium hydroxide monohydrate. *Cryst. Growth Des.* **2024**, *24*, 1235–1244. [CrossRef]
13. Galvanauskaitė, N.; Sulcius, A.; Griskonis, E.; Diaz-Arista, P. Influence of Te(VI) additive on manganese electrodeposition at room temperature and coating properties. *Trans. Inst. Met. Finish.* **2011**, *89*, 325–332. [CrossRef]
14. Ropp, R.C. Group 16 (O, S, Se, Te) alkaline earth compounds. In *Encyclopedia of the Alkaline Earth Compounds*; Elsevier: Amsterdam, The Netherlands, 2013; pp. 105–197. [CrossRef]
15. Zhao, L.Y.; Siu, A.C.; Leung, K.T. Anomalous electrodeposition of metallic Mn nanostructured films on H-terminated Si(100) at anodic potential. *Chem. Mater.* **2007**, *19*, 6414–6420. [CrossRef]
16. Ding, L.; Fan, X.; Du, J.; Liu, Z.; Tao, C. Influence of three N-based auxiliary additives during the electrodeposition of manganese. *Int. J. Miner. Process.* **2014**, *130*, 34–41. [CrossRef]
17. Selenium Toxicity-Nutritional Disorders-Merck Manual Professional Edition. Available online: <https://www.merckmanuals.com/professional/nutritional-disorders/mineral-deficiency-and-toxicity/selenium-toxicity> (accessed on 14 May 2025).
18. Pérez-Garibay, R.; Rojas-Montes, J.C.; Bello-Teodoro, S.; Flores-Álvarez, J.M. Effect of SeO₂ on the morphology of electrodeposited manganese. *J. Appl. Electrochem.* **2020**, *50*, 1291–1299. [CrossRef]
19. Xu, F.; Dan, Z.; Zhao, W.; Han, G.; Sun, Z.; Xiao, K.; Jiang, L.; Duan, N. Electrochemical analysis of manganese electrodeposition and hydrogen evolution from pure aqueous sulfate electrolytes with addition of SeO₂. *J. Electroanal. Chem.* **2015**, *741*, 149–156. [CrossRef]
20. Schlesinger, M.E. The Mn-Te (manganese-tellurium) system. *J. Phase Equilib.* **1998**, *19*, 591–596. [CrossRef]
21. Sharma, R.K.; Singh, G.; Shul, Y.G.; Kim, H. Mechanism of manganese (mono and di) telluride thin-film formation and properties. *Phys. B* **2007**, *390*, 314–319. [CrossRef]
22. Müller, R.; Zschiesche, W.; Steffen, H.M.; Schaller, K.H. Tellurium intoxication. *Klin. Wochenschr.* **1989**, *67*, 1152–1155. [CrossRef] [PubMed]
23. Xue, J.; Zhong, H.; Wang, S.; Long, D. Influence mechanism of sulfide ions during manganese electrodeposition. *J. Wuhan Univ. Technol. Mater. Sci. Ed.* **2019**, *34*, 1451–1459. [CrossRef]
24. Xue, J.R.; Zhong, H.; Wang, S.; Li, C.X.; Wu, F.F. Influence of tetraborate anions on manganese electrodeposition in an anion-exchange membrane electrolysis reactor. *Ionics* **2017**, *23*, 177–189. [CrossRef]
25. ASTM A283/A283M-03; Standard Specification for Low and Intermediate Tensile Strength Carbon Steel Plates. ASTM International: West Conshohocken, PA, USA, 2003. [CrossRef]
26. ASTM A36 vs ASTM A283 Steel Plate. Available online: <https://www.central-steels.com/newsdetail/astm-a36-vs-astm-a283-steel-plate.html> (accessed on 24 June 2026).
27. Surface Finish Recommendations for Seals. Available online: <https://kcseals.ca/the-impact-of-surface-finish-on-seal-performance/> (accessed on 24 June 2026).
28. Liu, Y.; Li, J.; Chen, Z.; Niu, X.; Liu, Z.; Wang, Z.; He, D. Effect of annealing temperature on microstructure and properties of stainless steel/copper composite strips. *Adv. Compos. Hybrid Mater.* **2026**, *9*, 103. [CrossRef]
29. Cai, G.; Huang, Y.; Misra, R.D.K. Effects of tempering temperature on microstructure and mechanical property of high-strength low-carbon steel through Nb, V and Ti microalloying. *J. Mater. Eng. Perform.* **2026**, *35*, 1–10. [CrossRef]
30. Liu, S.; Li, C.; Liu, G.; Yang, Y. Experimental study on solid dielectric electrochemical polishing for high-roughness metal additive manufacturing surfaces. *J. Mater. Res. Technol.* **2026**, *42*, 716–728. [CrossRef]
31. Wei, P.; Hileman, O.E.; Batani, M.R.; Deng, X.; Petric, A. Manganese deposition without additives. *Surf. Coat. Technol.* **2007**, *201*, 7739–7745. [CrossRef]
32. Sulcius, A.; Griskonis, E.; Kantminiene, K.; Zmuidzinavičienė, N. Influence of different electrolysis parameters on electrodeposition of gamma- and alpha-Mn from pure electrolytes-A review with special reference to Russian language literature. *Hydrometallurgy* **2013**, *137*, 33–37. [CrossRef]
33. Žmuidzinavičienė, N.; Griškonis, E.; Šulčius, A. The corrosion of Mn coatings electrodeposited from a sulphate bath with Te(VI) additive and influence of phosphate post-treatment on corrosion resistance. *Coatings* **2023**, *13*, 1617. [CrossRef]
34. Wang, S.; Wang, J.W.; Tian, J.Y.; Yang, P.; He, Y.; Yang, C.Y.; Wang, H.F. Effect of current density on growth law of manganese electrodeposition. *Russ. J. Electrochem.* **2023**, *59*, 616–627. [CrossRef]

35. Griškonis, E.; Šulčius, A.; Žmuidzinavičienė, N. Influence of temperature on the properties of Mn coatings electrodeposited from the electrolyte containing Te(VI) additive. *J. Appl. Electrochem.* **2014**, *44*, 1117–1125. [CrossRef]
36. Jensen, W.B. Faraday's laws or Faraday's law? *J. Chem. Educ.* **2012**, *89*, 1208–1209. [CrossRef]
37. Nuñez Pérez, F.A. Electrochemical analysis of corrosion resistance of manganese-coated annealed steel: Chronoamperometric and voltammetric study. *AppliedChem* **2024**, *4*, 367–383. [CrossRef]
38. Fang, L.; Xie, L.B.; Hu, J.; Li, Y.; Zhang, W.T. Study on the growth and corrosion resistance of manganese phosphate coatings on 30CrMnMoTi alloy steel. *Phys. Procedia* **2011**, *18*, 227–233. [CrossRef]
39. Spray Trication Zinc Phosphating-Phosphate Conversion Coatings. Available online: <https://web.archive.org/web/20110716164906/http://www.surfacepretreatment.com/default.asp?id=2> (accessed on 11 May 2025).
40. Мареграмов, А.М.; Рамазанов, М.А.; Гаджиева, Ф.В. Исследование структуры и диэлектрических свойств нанокмпозитов на основе полипропилена и наночастиц диоксида циркония. *Acta Educ.* **2025**, *2*, 4–9. [CrossRef]
41. Sodium tellurate. Available online: <https://www.smolecule.com/products/s1539916> (accessed on 19 May 2025).
42. Lide, D.R. (Ed.) *CRC Handbook of Chemistry and Physics*, 88th ed.; CRC Press: Boca Raton, FL, USA, 2007.
43. Konovalova, V. Effect of modifiers introduced into cold phosphating solutions on the physical and mechanical properties of the formed phosphate films. *MATEC Web Conf.* **2021**, *346*, 01034. [CrossRef]
44. Doerre, M.; Hibbitts, L.; Patrick, G.; Akafuah, N.K. Advances in automotive conversion coatings during pretreatment of the body structure: A review. *Coatings* **2018**, *8*, 405. [CrossRef]
45. Dhananjayan, N.; Banerjee, T. Crystallographic Modifications of Manganese and Their Transformation Characteristics. Available online: <http://eprints.nmlindia.org/5609> (accessed on 14 May 2025).
46. Duszczek, J.; Siuzdak, K.; Klimczuk, T.; Strychalska-Nowak, J.; Zaleska-Medynska, A. Manganese phosphatizing coatings: The effects of preparation conditions on surface properties. *Materials* **2018**, *11*, 2585. [CrossRef] [PubMed]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.