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Effect of current density on Ni-W coatings of SS316L current collectors for Na-S batteries

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Abstract

In this study, we investigated the effects of current density on the behavior of an amorphous Ni-W coating on a stainless steel 316 L (SS316L) surface. The performances of the Ni-W coatings and SS316L were studied through SEM, XRD and four-probe resistance tester. The corrosion resistance of the coating was determined through static corrosion tests in a sulfur environment at 350 °C. The amorphous Ni-W coating at different current densities slowed the corrosion rate and improved the conductivity of the SS316L current collector. At a current density of 15 A·dm⁻², the crystal structure of the Ni-W coating was densest. The corrosion rate of the coating was 0.0856 mm·y⁻¹, which was lower than that of SS316L (0.5123 mm·y⁻¹) after 72 h in a 350 °C molten sulfur environment, and the block resistance was 0.3312 mΩ, which was also lower than that of SS316L (0.3825 mΩ).

1. Introduction

Sodium-sulfur batteries have applications in energy industries, and have become one of the most promising static energy storage batteries owing to their superior characteristics [1, 2]. The working temperature of sodium-sulfur batteries is 350 °C. The electrode material remains molten at this temperature, and the electrical energy is converted into chemical energy [3–6]. However, the current collector can be easily corroded in this environment, which causes capacity loss and safety problems for Na-S batteries [7, 8]. Many metals, such as Fe, Ni, and Cr, react with sulfur and sodium polysulfide to produce sulfides, which reduce the content of the active electrode materials. Thus, a key issue for Na-S batteries is developing current collectors with a strong corrosion resistance without sacrificing conductivity [9–11]. Metallic Cr and Mo are widely used as high-temperature current collectors with good corrosion resistance; however, they are very expensive. The high cost can be offset by using expensive materials as thin coatings on cheaper substrates, such as stainless steel [12].

SS316L is widely employed as a current collector for batteries owing to its thermal expansion rate and lower block resistance [13]. However, owing to the limitation of SS316L, that cannot maintain good corrosion resistance in a long-term sodium-sulfur environment at high temperatures, SS316L cannot be directly used as a current collector for Na-S batteries.

The properties of SS316L can be improved using various coatings such as, Cu [14], Cr₂O₃ [15], Ni [16], Ti₆Al₄V [17], polyaniline [18], and TiN [19]. However, most of these methods have certain drawbacks. Chromium coatings are widely used for the protection of metal surfaces because they have the ability to withstand corrosion and wear [20–23]; however, the chromium plating process often leads to environmental pollution. Recently, the preparation of Ni-based coatings by electrodeposition has received increasing attention [24]. In contrast to chromium coating, Ni–W electrodeposition can reduce environmental pollution and produce a coating with superior performance [25–28]. Allahyarzadeh et al [29, 30] prepared a Ni–W–Al₂O₃ coating with a functionally graded microstructure and a Ni–W-alumina nanocomposite coating. The coatings doped with adequate amounts of Al₂O₃ could effectively improve the performance of the coating; furthermore, increasing the pulse frequency contributed to an increase in the corrosion resistance of the Ni–W–Al₂O₃ coatings. Zhang et al [31] prepared a Ni–W–Ce coating on a stainless steel surface that
greatly improved the corrosion resistance. The improved performance of the coating was associated with the addition of Ce; however, the addition of rare earth elements increased the cost, material waste and environmental pollution. Reports of various coatings on stainless steel and their characteristics in high-temperature sulfur environments are shown in Table 1.

Karahan et al[32] conducted a study on the preparation of conductive polymer films on steel substrates by electroplating. The current density affected the properties of the coating; the performance of the coating was optimal at 2 mA cm⁻². Monev et al[33] reported the morphology and performance of galvanic Au–Ni alloy coatings. The coatings prepared under different current densities had different morphologies and Ni content; furthermore, at higher current densities, the coating become rougher. Jesmani et al[34] reported the influence of current density on Ni-Mo coatings; they found that the current density could alter the Mo content and an increase in current density could form an amorphous coating.

According to previous studies, current density can change the structures and properties of coatings; however, the effect of current density on the surface modification of Ni-W coatings on the current collector of Na-S batteries has not been explored. In this work, a Ni-W coating was deposited onto SS316L via an electroplating method. The effects of current density on the microstructures and properties of these coatings were investigated.

Table 1. Characteristics of various materials in high temperature sulfur environments.

| Coating          | Characteristic                                                                 | Source |
|------------------|-------------------------------------------------------------------------------|--------|
| Cu               | The coating cannot form a protective film in a high-temperature sulfur environment | [14]   |
| Cr₂O₃,Polyaniline| The conductivity of the coating is poor                                       | [15, 18]|
| Ni               | The coating easily forms corresponding sulfide                                | [16]   |
| Ti₆Al₄V,TiN      | Higher cost and not easy to deform                                            | [17, 19]|
| Ni-W             | Good corrosion resistance and good electrical conductivity                    | [31]   |

Table 2. Chemical analysis of SS316L used in this work.

| Element | Fe    | Cr    | Mn    | Ni    | C    | Si    | Al    |
|---------|-------|-------|-------|-------|------|-------|-------|
| Content%| bal   | 17.42 | 0.893 | 11.380| ≤0.08| 0.709 | 0.142 |

Table 3. Corrosion grade corresponding to corrosion rate of metal materials.

| Corrosion rate (vt/\,mm\,\cdot\,y⁻¹) | Corrosion grade                      |
|-------------------------------------|--------------------------------------|
| <0.001                             | Completely corrosion-resistant material |
| 0.001–0.01                          | Highly corrosion-resistant material |
| 0.01–0.1                            | Corrosion-resistant material         |
| 0.1–1.0                             | Generally corrosion-resistant material |
| 1.0–10                              | Slightly corrosion-resistant material |
| >10                                 | Non-corrosion-resistant material     |
2. Experimental

2.1. Synthesis
The coatings were electrodeposited on SS316L (50 × 25 × 2 mm³). Table 2 lists the chemical composition of SS316L. The electrodeposition conditions and electrolyte composition have been described in detail elsewhere [31]. The current densities for deposition were 10, 12, 14, 15, 16, 18, and 20 A dm⁻².

2.2. Characterization
We calculated the corrosion rate of the sample through a static corrosion experiment and evaluated its corrosion resistance in terms of a ‘corrosion grade,’ as shown in table 3.

Figure 1 shows a simple schematic of the static corrosion experiment used to test the corrosion-resistance capability of SS316L and coatings in molten sulfur at 350 °C.

After 72 h, the samples were removed and washed via ultrasound in carbon disulfide and ethanol solution. Finally, the samples were dried using a blower. The corrosion rate of the samples was calculated according to equations (1) and (2). The corrosion test was repeated five times to improve test accuracy.

\[
\nu_c = \frac{w_2 - w_1}{s \times t} \tag{1}
\]

\[
\nu_t = \frac{8.76 \times v_i}{\rho_s} \tag{2}
\]

The corrosion rates \(\nu_c\) (g·m⁻²·h⁻¹) and \(\nu_t\) (mm·y⁻¹) were calculated, where \(w_1, w_2, s, t, \) and \(\rho_s\) are, the mass of the sample before corrosion (g), mass of the sample after corrosion (g), superficial area of the sample (cm²), corrosion time (h), and density of samples (g·cm⁻³), respectively. The crystal structures of the coatings before and after corrosion were determined using x-ray diffraction (XRD; Rigaku, Japan), in which the 2θ range was set from 5° to 90° at a speed of 10°·min⁻¹. The morphologies of the coatings and corrosion products were observed using scanning electron microscopy (SEM; JSM-6360 and ULTRA™55). The resistance of each sample was measured through four-probe measurement (RTS-9). To determine the grain size of the coatings, the experimental data were processed using the Scherrer equation (3).

\[
D = \frac{K\lambda}{\beta \cos \theta} \tag{3}
\]

where \(K\) is a constant with a value of 0.943; \(\lambda\) is the wavelength of the x-ray; \(\beta\) is the full width at half maximum of the diffraction peak; and \(\theta\) is the diffraction angle.

The Ni-W coatings (1 cm × 1 cm) were evaluated by an atomic force microscopy (AFM; NT-MDT Prima) in air (temperature of 25 °C; relative humidity of 25%). The roughness was automatically assessed as a numeric value using the Nanoscope Analysis software.

The bonding force of the Ni-W coatings was tested using the scratch method. Scratches on the Ni-W surface were made by applying pressure with a knife held at an angle of approximately 45% to the surface. The distance between each scratch was approximately 1 mm, and a constant traction was applied to the coating with a tape to determine whether the coating falls off.

Figure 2. SEM image of SS316L after 72 h corrosion in a 350 °C sulfur environment.
3. Results and discussions

3.1. Corrosion behavior of the SS316L

The block resistance of plain SS316L was 0.3825 mΩ and the corrosion rate was 0.5123 mm·y⁻¹ after 72 h of corrosion in a 350 °C molten sulfur environment. Therefore, SS316L cannot be used directly as a current collector material for Na-S batteries. According to table 3, SS316L is a 'generally corrosion-resistant material' in this environment.

Figure 2 shows the SEM image of the SS316L substrate after 72 h of corrosion. The substrate was severely corroded in this environment, and the surface was covered with a layer of loose substance, which could not prevent further corrosion of the substrate. As shown in figure 3, the main corrosion products are iron sulfide and chromium sulfide.

3.2. Composition and microstructure analysis of the coating

The XRD spectra of the Ni-W coatings deposited at various current densities are shown in figure 4. The broadening of the XRD peaks indicated that the phase of the Ni-W coating was amorphous. An appropriate
current density could slightly increase the peak width of the Ni-W coatings, which was an indication of reduced grain size. The grain sizes of the coatings obtained at different current densities were calculated according to the Scherrer equation (3), and are listed in Table 4. The minimum grain size was 31 nm at 15 A·dm$^{-2}$. The current density...
density effectively controlled grain refinement by inhibiting crystal growth and reducing the influence of hydrogen evolution reaction during the electrodeposition process.

Figure 5 shows the SEM images of the coating surfaces at different current densities. The surface morphology of the Ni-W coating at 10 A·dm⁻² is shown in figure 5(a), where the granular size was spherical and did not form a dense coating. At 12 A·dm⁻² the particles adhered to the substrate with observable cracks, and the surface of
the coating was uneven (figure 5(b)). At 14 A·dm$^{-2}$ the surface morphology became denser, but there were still many cracks (figure 5(c)). At a current density of 15 A·dm$^{-2}$, the Ni-W coating became regular and smooth, and the surface structure of the coating was complete and dense (figure 5(d)). The surface morphology of the Ni-W coatings had more serious flaws when the current densities were 16 A·dm$^{-2}$ (figure 5(e)), 18 A·dm$^{-2}$ (figure 5(f)) and 20 A·dm$^{-2}$ (figure 5(g)); there were cracks and black impurities at the grain boundaries. During the preparation of Ni-W alloys, low current densities reduced the electrodeposition rate of the coating, and excessively high current densities exacerbated the hydrogen evolution reaction; moreover, the effect of hydrogen embrittlement became more serious [35].

### 3.3. Surface roughness analysis

Figure 6 shows height images with roughness of Ni-W coatings that were deposited at various current densities. It was observed that the current density has a significant influence on the roughness of the Ni-W coating. As the current density increased, the surface roughness of the coating first increased and then decreased. Table 5 lists the coating roughness parameters deposited at various current densities. When the current density was less than 15 A·dm$^{-2}$, a deep valley appeared on the surface. When the current density was 10 A·dm$^{-2}$, $R_a$ reached a minimum value of 86.3 nm and $R_{max}$ was 751 nm. When the current density was 15 A·dm$^{-2}$, $R_a$ reached a

![Image](image_url)

**Figure 7.** Adhesion test chart of Ni-W coatings prepared at different current densities ((a) 10 A·dm$^{-2}$; (b) 15 A·dm$^{-2}$; (c) 20 A·dm$^{-2}$).

**Table 5.** Surface roughness of Ni-W coatings deposited at various current densities.

| Current density/A·dm$^{-2}$ | $R_a$  | $R_{q}$ | $R_{max}$ |
|-----------------------------|--------|---------|-----------|
| 10                          | 86.3   | 110     | 751       |
| 12                          | 77.5   | 94.9    | 623       |
| 14                          | 60.8   | 76.3    | 616       |
| 15                          | 43.4   | 54.3    | 452       |
| 16                          | 58.3   | 74.1    | 521       |
| 18                          | 76.5   | 98.2    | 724       |
| 20                          | 103    | 126     | 808       |
minimum value of 43.4 nm and an $R_{\text{max}}$ of 452 nm. As the current density increased, the degree of electrochemical polarization increased, whereas the nucleation rate increased, and the surface roughness decreased.

When the current density was 20 A·dm$^{-2}$, $R_a$ reached a maximum value of 103 nm and $R_{\text{max}}$ was 808 nm. When the current density exceeded 15 A·dm$^{-2}$, the crystals that produced by electrodeposition were coarse because the cathode hydrogen evolution reaction was more serious.

3.4. Adhesion to the substrate

Figure 7 shows images the coatings after the scratch test. The coatings prepared at different current densities did not fall off. The coating adhered even when parts of the substrate were exposed, and thus the bonding force of the plating layer was qualified.

3.5. Corrosion analysis

The corrosion rates of the Ni-W coatings prepared at different current densities, after 72 h in a 350 °C sulfur environment are shown figure 8. The minimum corrosion rate was 0.0856 mm·y$^{-1}$ at 15 A·dm$^{-2}$, which is an order of magnitude smaller than that of plain SS316L, indicating that the Ni-W coating was a corrosion-resistant material in the molten environment. The presence of tungsten metal effectively prevented the iron in the substrate from converting to iron sulfide [36]. According to the surface morphology and roughness of the coating, the surface morphology of the coating directly affects its corrosion resistance; the rougher the coating surface, the more exposed it is to the corrosive environment.

Figure 9 shows XRD patterns of Ni-W coatings prepared at different current densities, after 72 h in a 350 °C sulfur environment. Between 14 A·dm$^{-2}$ and 16 A·dm$^{-2}$, the XRD showed mainly amorphous diffraction peaks.
of the Ni-W coating. A small amount of NiS$_2$ diffraction peaks indicated that a part of Ni in the Ni-W coating reacted with sulfur at 15 A·dm$^{-2}$. When the current density was less than 14 A·dm$^{-2}$ and greater than 16 A·dm$^{-2}$, the coating was damaged, and sulfides such as WS$_2$, NiS$_2$, and Ni$_3$S$_4$ appeared with a significant increase in NiS$_2$ content. This was because the coating was not dense and the nickel element of the Ni-W coating was more likely to react with sulfur in the high-temperature environment to form sulfide.

Figure 10. SEM images of Ni-W coatings deposited at various current densities after 72 h corrosion in a 350 °C sulfur environment ((a) 10 A·dm$^{-2}$; (b) 12 A·dm$^{-2}$; (c) 14 A·dm$^{-2}$; (d) 15 A·dm$^{-2}$; (e) 16 A·dm$^{-2}$; (f) 18 A·dm$^{-2}$; (g) 20 A·dm$^{-2}$).
The standard electrode potentials of Fe, Ni, and S are listed in Table 6. The Gibbs free energy was calculated using formulas (4) and (5).

$$\Delta G = -nFE_{\text{rxn}} = -nF(\varphi_+ - \varphi_-)$$  \hspace{1cm} (4)

$$\Delta G = \Delta H - \Delta (TS)$$  \hspace{1cm} (5)

where $\Delta G$, $n$, $F$, $E_{\text{rxn}}$, $\Delta H$, $T$, and $S$ are, the Gibbs free energy, amount of substance that transfers charge (mol), Faraday constant (95486.70 C·mol$^{-1}$), standard electrode potential (V), change in enthalpy, temperature, and entropy, respectively.

$$\text{Fe}^2+ + 2e^- \rightarrow \text{Fe}$$  \hspace{1cm} $-0.44$

$$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$$  \hspace{1cm} $-0.257$

$$S + 2e^- \rightarrow S^{2-}$$  \hspace{1cm} $-0.447$

Reactions (6)–(8) are the main chemical equations of the SS316L, Ni-W coating and sulfur at high temperatures, respectively. Because the standard electrode potential of S is less than 0 ($E^0_S < 0$), S could cause the reaction to proceed at 350 °C. The iron was more likely convert to iron sulfides than nickel to nickel sulfides in a molten sulfur environment.

Figure 10 shows surface morphology images of Ni-W coatings deposited at different current densities after 72 h corrosion in a 350 °C sulfur environment. The corrosion products became spherical at 10 A·dm$^{-2}$, 12 A·dm$^{-2}$, and 14 A·dm$^{-2}$ (figures 10(a)–(c)). Meanwhile, Needle-like products also formed on the surface of the coatings. The needle-like and spherical products were NiS$_2$ according to XRD analysis. The coating structure remained dense at 15 A·dm$^{-2}$ (figure 10(d)). This indicates that the Ni-W coating had excellent corrosion resistance. The structure of the Ni-W alloy coating was in the form of a replacement solid solution, in which tungsten was a solute atom and nickel was a solvent atom. The chemical bond of Ni-W alloy was relatively stable at 350 °C. The Ni-W coating played a significant role in protecting the SS316L in a 350 °C sulfur environment, which prevented the molten sulfur from reacting with Fe. According to figures 10(e)–(g), a loose surface structure of nickel sulfide and iron sulfide can be observed.
3.6. Block resistance analysis

Figure 11 presents the block resistances of Ni-W coatings deposited at various current densities after 72 h of corrosion in a 350 °C sulfur environment. It could be seen that the block resistance value increased slightly after corrosion because of the formation of sulfides on the surface of the substrate. The block resistance of the coatings ranged from 0.33 mΩ to 0.36 mΩ. With an increase in the current density, the value of the block resistance of the coating first decreased and then increased. At a current density of 15 A·dm$^{-2}$, the block resistance of the coating was the smallest (0.3312 mΩ). These results show that the coating had good stability in a sulfur environment at 350 °C. The Ni-W coating exhibited adequate corrosion resistance and could meet the requirements of the current collector for a Na-S battery.

4. Conclusions

The corrosion rate of plain SS316L was 0.5123 mm·y$^{-1}$ and the block resistance was 0.3825 mΩ after 72 h in a 350 °C molten sulfur environment. The corrosion resistance of the coatings prepared using different currents was superior to that of SS316L under the same conditions. The surface structure of the Ni-W coating was complete and dense at 15 A, which slowed down the corrosion rate and improved the conductivity of SS316L. Additionally, the morphology after corrosion was superior. The corrosion rate was 0.0856 mm·y$^{-1}$, and the block resistance was 0.3312 mΩ.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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