Corrosion behavior of ZnO nanosheets on brass substrate in NaCl solutions

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\textbf{Abstract}
The \textit{in situ} growth of ZnO nanosheets has been demonstrated by our research group and the excellent electrical contact between the ZnO nanosheets and brass substrate enables many potential applications in gas sensing and photocatalytic degradation. However, problems arising from corrosion, especially that arising from chloride ions, are inevitable in the field. In this work, the corrosion behavior of these ZnO nanosheets is investigated in chloride solutions. Our results show that in a NaCl solution, the chloride ions can react with ZnO to form ZnCl\textsubscript{2}. When the NaCl concentration is relatively low (1 wt%), the structure exhibits a strong passivation behavior but a higher concentration of chloride ions can accelerate the transformation from ZnO to ZnCl\textsubscript{2}. The results also disclose that a high concentration of NaCl weakens the passivation performance and when the concentration reaches 3 wt%, the passivation ability vanishes completely.

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\section{1. Introduction}
Zinc oxide (ZnO) possesses many unique properties including photoelectric conversion, high piezoelectricity, and good biocompatibility and are potentially useful in applications involving solar cells \cite{1,2}, piezoelectric nanogenerators \cite{3,4}, gas sensors, and biosensors \cite{5–7}. Nanostructured ZnO which has attracted increasing attention due to their high aspect ratio and surface-to-volume ratio \cite{8,9} exhibits high sensitivity and high efficiency when used as gas sensors or photoelectrochemical devices. In our previous work \cite{10}, ZnO nanosheets (ZnO NSs) were fabricated \textit{in situ} on Cu\textsubscript{0.66}Zn\textsubscript{0.34} brass substrate using a convenient and economical method. The conducting brass substrate provides excellent electrical contact serving as the electrode in a ZnO-based gas sensor. Compared to ZnO powders, these ZnO NSs can protect the solutions from secondary pollution in photocatalytic degradation processes. However, corrosion is encountered in these applications and it is important to investigate the corrosion behavior of the nanostructure in an aggressive environment such as an aqueous medium containing chloride ions. In the work reported here, the corrosion behavior of ZnO NSs on brass in solutions containing different concentrations of NaCl is investigated and the corroded surfaces are characterized to elucidate the factors affecting the anti-corrosion characteristics of the nanostructures.

\section{2. Experimental details}
A commercial available Cu\textsubscript{0.66}Zn\textsubscript{0.34} sheet was cut into 10 mm × 10 mm × 2 mm coupons. The samples were ground and polished followed by ultrasound cleaning in alcohol. Uniform ZnO NSs were then fabricated \textit{in situ} by the method described in Ref. \cite{10}. The phase constituents of the ZnO NSs were determined by X-ray diffraction (XRD). The morphologies of the samples before and after electrochemical tests were monitored by SEM (SEM, Hitachi S4700) and energy-dispersive X-ray spectroscopy (EDS) was employed to determine the elemental compositions in selected regions.

The corrosion behaviors of brass with and without ZnO NSs were investigated by potentiodynamic polarization and open circuit potential evolution (OCP) in NaCl solutions. 1, 2 and 3 wt\% NaCl solutions, were adopted to disclose the influence of NaCl concentrations on the corrosion behavior of ZnO NSs coated brass.

The electrochemical tests were carried out using a model 363 potentiostat/galvanostat (EG\&G Princeton Applied Research). A three-electrode cell consisting of the sample as the working electrode, graphite rod as counter electrode, and calomel electrode (SCE) as the reference electrode was adopted. A 2 mV s\textsuperscript{-1} scanning rate and a potential range from –1 to 2 V were used in the potentiodynamic polarization test. The corrosion potential (E\textsubscript{corr}) and corrosion current density (I\textsubscript{corr}) were determined using the Tafel fit. In the open circuit potential (OCP) measurement, changes in the open circuit potential (E\textsubscript{corr}) were monitored as a function of immersion time for about 20 ks. The data were recorded every 2 s. All the electrochemical tests were performed at room temperature.

\section{3. Results and discussion}
The XRD results acquired from the ZnO NSs on brass in Fig. 1 show the presence of ZnO with good crystallinity. Fig. 2 shows the surface morphology of ZnO NSs. The ZnO has a fine nanosheet...
structure with a thickness of tens of nanometers and width of hundreds of nanometers.

The potentiodynamic polarization curves of the brass substrate with and without the ZnO NSs in 1, 2 and 3 wt% NaCl solutions are shown in Fig. 3. The corrosion current density ($I_{corr}$) and corrosion potential ($E_{corr}$) values determined from the polarization curves are listed in Table 1. No obvious enhancement in the corrosion potentials is observed from the ZnO NSs coated brass in all three solutions can be observed compared to pure brass. The corrosion current densities of the two sets of samples in the three solutions are similar as well. However, it should be noted that in the anodic polarization stage, when the polarization potential reaches a certain value, the current densities of the ZnO NSs coated brass are much lower than those of the uncoated brass. As soon as the ZnO NSs coated brass experiences anodic polarization, a much lower corrosion rate is observed than pure brass. With increasing NaCl concentrations, the corrosion potential and corrosion current density of the ZnO NSs coated brass change insignificantly. In the 1 wt% NaCl solution, the ZnO NSs coated brass exhibits a strong passivation behavior. In contrast, in the 2 wt% NaCl solution, the passivation behavior weakens and when the concentration reaches 3 wt%, the passivation behavior disappears almost entirely.

The OCP results acquired from the samples in 1, 2, and 3 wt% NaCl solutions are presented in Fig. 4. The corrosion potentials of the ZnO NSs coated brass in the three solutions are all much more positive than that of pure brass during the entire exposure duration. No intense fluctuations in the potentials can be observed from both sets of samples in the three solutions can be observed.
Table 1  
Electrochemical response of uncoated and ZnO NSs coated brass in aqueous NaCl solutions.

<table>
<thead>
<tr>
<th>Samples</th>
<th>1%</th>
<th>2%</th>
<th>3%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{corr}$ (mV)</td>
<td>$I_{corr}$ ($\mu$A cm$^{-2}$)</td>
<td>$E_{corr}$ (mV)</td>
</tr>
<tr>
<td>Brass</td>
<td>$-254.8$</td>
<td>$22.68$</td>
<td>$-289.84$</td>
</tr>
<tr>
<td>ZnO NSs coated brass</td>
<td>$-292.62$</td>
<td>$11.41$</td>
<td>$-288.12$</td>
</tr>
</tbody>
</table>

Fluctuations would be an indication that it is difficult for electrode at the electrode/solution interface to achieve equilibrium [11]. Although the smooth curves suggest a general corrosion process for all the samples in the three solutions, the two sets of samples exhibit different behaviors in the solutions. During the early stage, the potential of the ZnO NSs coated brass moves to a negative direction gradually and then remains nearly constant during subsequent immersion. The initial decrease in the corrosion potential is probably related to the penetration of aggressive ions. After some time, ion absorption from the solution by the ZnO NSs is saturated leading to a stable corrosion potential. The behavior of brass in the three solutions is similar. However, during the immersion period, a gradual cathodic polarization process is observed on brass in the three solutions. This may be related to the Zn dealloying process during corrosion of brass.

Dealloying, a common phenomenon in corrosion of alloys, is a process during which an element selectively segregates from an alloy. Generally, the more active element preferentially departs from the surface [12,13]. In brass, Zn possesses a more negative standard potential compared to Cu and preferentially dissolves in the solution. The gradual dissolution of Zn enlarges the area of pure Cu on the surface. Compared to pure brass, the complex potentials of Cu and brass are more negative. Thus, with the dissolution of Zn, the potential moves to a negative direction gradually.

Fig. 5 shows the surface morphologies of the brass substrate as well as ZnO NSs covered brass after the potentiodynamic polarization tests in the three NaCl solutions. The morphologies of pure brass after immersion in the three solutions are similar and show a typical porous structure. As aforementioned, corrosion of brass is usually in the form of dezincification. Formation of a porous morphology is common in the dealloying process. In the 1 wt% NaCl solution, the anodic polarization process creates the black regions. The EDS results reveal that some ZnCl$_2$ forms in these regions but no Cu can be observed indicating that there are no corrosion pits. High magnification views of the white area show that the original ZnO NSs are retained quite well in the 2 wt% NaCl solution, the number of black area increases dramatically but in the other regions, the nanosheet pattern is well retained. In the 3 wt% NaCl solution, the nanosheet vanishes totally leaving behind a rough surface. EDS results indicate that these regions also contain high contents of ZnCl$_2$. The results show that chloride ions in an aqueous solution attack the ZnO NSs forming ZnCl$_2$ and the degree of corrosion depends on the NaCl concentration. A higher chloride ion concentration accelerates the reaction with ZnO. Hence, during applications in the field, it is imperative that these ZnO nanostructures are shielded from a high concentration of chloride ions of 3% or higher, e.g., 3.5 wt% in seawater, otherwise extensive corrosion results rendering complete dissolution of the nanosheets.
Fig. 5. SEM images of brass after potentiodynamic polarization experiments in NaCl solutions with different concentrations: (a), (c) and (e) are brass in 1, 2 and 3 wt% NaCl solutions, respectively; (b), (d) and (f) are ZnO NSs coated brass in 1, 2 and 3 wt% NaCl solutions, respectively; (b1), (d1) and (f1) are EDS results obtained from the corresponding areas in (b), (d), and (f), respectively.
4. Conclusion

The corrosion characteristics of ZnO NSs fabricated on brass are evaluated in aqueous solutions with different concentrations of NaCl. Compared to the corrosion behavior of pure brass, the corrosion resistance of the ZnO NSs coated brass is enhanced. The ZnO coated brass does not exhibit pitting corrosion in the NaCl solutions. When the NaCl concentration is low, a strong passivation behavior is observed from the ZnO NSs coated brass. However, when the chloride concentrations increases, the passivation effects diminish and when it reaches 3%, complete dissolution of the ZnO NSs is observed. Hence, it is important that these ZnO nanostructures are not subject to a concentration of chloride ions of 3% or higher.

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