Corrosion Behavior of Brass In TiO$_2$ Nanofluids

Kai Wu, Hong-Hua Ge*, Feng Wang and Hong-Wang Zhou

Shanghai University of Electric Power, Shanghai Engineering Research Center of Energy-Saving in Heat Exchange Systems, Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, Shanghai 200090, China

E-mail: gehonghua@shiep.edu.cn

Abstract. Corrosion behavior of brass electrode in TiO$_2$ nanofluids was analyzed using electrochemical impedance spectroscopy. The experimental results show that TiO$_2$ nanoparticles promote corrosion of brass. The corrosion resistance of brass electrode decreases with the increase of the temperature of the TiO$_2$ nanofluids. Sodium dodecyl benzene sulfonate (SDBS) is a dispersant in nanofluids and also appears corrosion inhibition to brass, and the corrosion inhibition enhances with the increase of SDBS concentration. The corrosion resistance of brass in TiO$_2$ nanofluids would decrease when the concentration of dispersant SDBS exceeds a certain value.

1. Introduction

With the development of thermal science and technology, the traditional heat transfer medium in the manufacturing, metallurgy, energy, transportation and microelectronics has been difficult to meet the increasing heat transfer load and heat transfer intensity, so the efficiency of the heat transfer system put forward higher requirements. An effective method for improving the heat transfer efficiency of the liquid is to add metal, non-metal or polymer solid particles to the base liquid. Because the thermal conductivity of solid particles is several orders of magnitude larger than that of liquids, the thermal conductivity of the two-phase fluid with solid particles is much larger than that of pure liquids. However, there are many problems in practical application, such as large particles, easy settlement, easy to produce clogging and abrasion, which limits its application in industry.

In 1995, Choi et al.[1] at Argonne National Laboratory in the United States, first proposed the concept of nanofluid, which refered to the formation of nano-sized metal or non-metallic particles in liquid medium in a certain way and proportion to form stable, high thermal conductivity of the new heat transfer medium, which was used in thermal engineering nanotechnology in this traditional field of innovative research. In recent years, nano-fluid had become one of the hot spots in heat transfer and material research because of its high thermal conductivity[2-4], small wall friction and good optical properties[5].

In recent years, people began to pay attention to the corrosion of metals in nano-fluids. However, the results from different systems were not consistent, nanoparticles inhibited the corrosion of metals in some systems and promoted the corrosion of metals in other systems, and most of the above researches were taken in distilled water system.

Deionized water or organic solvent as the base fluid were often used in the past to research the stability of nanofluids[6,7]. However, the application of nanofluids in cooling water systems in the industrial production has a good prospect in the future because of the significant energy-saving efficiency. TiO$_2$ nanofluid is an economical and effective nanofluid, and it is one of the main...
researched nanofluids. So TiO₂ nanofluids were prepared using a simulated cooling water and corrosion of brass in the TiO₂ nanofluids were analyzed in this paper.

2. Experimental

2.1. Test solution and materials
Simulated cooling water (SCW), SDBS and nano TiO₂ were used to produce the nanofluids. Simulated cooling water consisted of 20 mg/L Ca²⁺, 6 mg/L Mg²⁺, 360 mg/L SO₄²⁻, 300 mg/L Cl⁻, 379 mg/L Na⁺, 122 mg/L HCO₃⁻[8]. The TiO₂ nano particles (diameter of 5-10 nm, purity > 99.8%) and SDBS (purity > 99.8%) were purchased from Aladdin Industrial Corporation (Shanghai, China).

2.2. Nanofluids preparation
SCW based TiO₂ nanofluid were prepared by two-step. TiO₂ was added to the solution, and then it was ultrasonically agitated and homogeneously dispersed in the solution.

2.3. Measurement of EIS
The working electrodes (1cm×1cm) were prepared from brass (type HSn70-1) and embedded in epoxy resin. Before the tests, all electrodes were mechanically polished by silicon carbide (SiC) paper progressively up to 2000 grid, degreased with alcohol and rinsed with distilled water. A saturated calomel electrode (SCE) and a latinum electrode were used as the reference and the auxiliary electrodes, respectively. Electrochemical Workstation CHI660E was used to measure the electrochemical impedance (EIS). All the experiments were performed at 30 ± 1°C.

3. Results and discussion

3.1. Corrosion behavior of brass in TiO₂ nanofluids

3.1.1. The effect of temperature and TiO2 nanoparticles
The influence of temperature on the corrosion behavior of brass was studied in both SCW and TiO₂ nanofluids. Nyquist plots of brass electrode in both systems were showed in figure 1. The fitting of electrochemical impedance spectroscopy was based on equivalent circuit in figure 2, where R_s is the solution resistance, R_t denotes the charge-transfer resistance and CPE is the constant phase angle element which explains the depression of the capacitance semi-circle. The fitting results display in table 1.

![Figure 1](image_url)

**Figure 1.** Nyquist plots of brass electrode in simulated cooling water and in TiO₂ nanofluids at different temperatures. SCW: (1) 30°C; (2) 40°C; (3) 50°C. TiO₂ nanofluids: (4) 30°C; (5) 40°C; (6) 50°C.
From table 1, it can be found that charge transfer resistance was largest at 30°C in both SCW and TiO\textsubscript{2} nanofluids. With the increase of temperature, the charge transfer resistance of the electrode/electrolyte interface decreased, indicating that corrosion resistance of brass reduced with the increase of temperature, which might be due to the accelerated diffusion of ion and destroyed the protection film of hydroxide ion. Comparing the data in table 1, the $R_{ct}$ value of brass in TiO\textsubscript{2} nanofluids were smaller than in SCW, which means that TiO\textsubscript{2} nanoparticles promote the corrosion. This is due to the Brownian motion between the nanoparticles and the local convective motion of the liquid produced by Brownian motion, which enhances the mass transfer rate of O\textsubscript{2}[9]. Therefore, TiO\textsubscript{2} nanoparticles exist alone in simulated cooling water, the probability of contact between O\textsubscript{2} and the brass surface increases, which may promote the corrosion of brass. The local convection caused by nanoparticles also promoted the diffusion of corrosion products.

3.1.2. Comparison the corrosion behavior of brass in different solution system
Due to the poor dispersibility of nanoparticles in aqueous solutions, SDBS is usually added to improve the dispersion of nanoparticles in solution. In this work, SDBS as disperser was entered into SCW. The experimental conditions were reported in table 2. Nyquist plot of brass in the three test systems at 30 °C were showed in figure 3. The fitting results were showed in table 3.

**Table 2.** The composition of the three test systems

| Test systems | TiO\textsubscript{2} (wt.% | SDBS (wt.% |
|--------------|-----------------|-----------------|
| 1-SCW        | 0               | 0               |
| 2-SCW + TiO\textsubscript{2} | 0.1   | 0               |
| 3-SCW + SDBS | 0               | 0.05            |

**Table 3.** The fitting results of figure 3

| Test systems | $R_s$ (Ω·cm\textsuperscript{2}) | $R_{ct}$ (kΩ·cm\textsuperscript{2}) | CPE $Q(\mu\Omega^{-1}·cm^{-2}·s^n)$ | n |
|--------------|-------------------------------|-----------------------------------|-----------------------------------|---|
| 1            | 167.0                         | 16.82                             | 88.32                             | 0.65 |
It showed in figure 3 and table 3 that $R_{ct}$ of brass in the TiO$_2$ nanofluids was minimal, indicating that corrosion of brass in TiO$_2$ nanofluids was most serious, probably due to the promotion of the mass transfer of O$_2$ and corrosion products. Brownian motion between TiO$_2$ nanoparticles and local convection of liquid produced by Brownian motion could enhance the mass transfer rate of O$_2$, which had mentioned above. When SDBS was added into the simulated water, the $R_{ct}$ value of the brass electrode increased from 16.82 kΩ·cm$^2$ to 36.23 kΩ·cm$^2$, indicating that SDBS had good corrosion inhibition effect on brass. As a commonly used surfactant, SDBS could adsorb on metal surface to form a protection layer against corrosion [10].

3.2. Effect of dispersant SDBS on brass

In order to further explore the corrosion inhibition effect of SDBS, different SDBS concentrations were performed in this paper. Nyquist plots of brass at 30 °C in TiO$_2$ nanofluids with different concentrations of SDBS were displayed in figure 4, and the fitting result in table 4.

![Figure 4. Nyquist plot of brass electrodes in TiO$_2$ nanofluids with different concentrations of SDBS](image)

Table 4. Fitting results of figure 4

| Test systems | $R_s$ (Ω·cm$^2$) | $R_{ct}$ (kΩ·cm$^2$) | CPE Q(μΩ$^{-1}$·cm$^{-2}$·sn) | n |
|--------------|-----------------|---------------------|-----------------------------|---|
| 1            | 167.0           | 16.82               | 88.32                       | 0.65 |
| 2            | 162.2           | 26.81               | 63.79                       | 0.68 |
| 3            | 156.0           | 30.89               | 53.96                       | 0.57 |
| 4            | 150.7           | 29.43               | 62.30                       | 0.68 |
| 5            | 151.6           | 27.42               | 72.93                       | 0.66 |

It could be seen from figure 4 and table 4 that the addition of dispersant SDBS increased the $R_{ct}$ of brass electrode in the TiO$_2$ nanofluids, indicating that SDBS had a good corrosion inhibition effect on brass in the water-based nano-fluid. When the concentration of SDBS reached 0.01%, the impedance
value of brass electrode decreased, which indicated that when the amount of dispersant SDBS exceeded a certain value, the corrosion inhibition to brass decreased, which may be related to the threshold effect of SDBS\textsuperscript{[11]}.

4. Conclusions
(1) The corrosion resistance of brass electrode in nanofluids decreased with the increase of temperature. The increase of temperature could promote the corrosion of brass in SCW and TiO\textsubscript{2} nanofluids.
(2) The addition of TiO\textsubscript{2} nanoparticles in the nanofluids promoted the corrosion of the brass, and the SDBS could effectively inhibit the brass corrosion.
(3) The inhibition effect of SDBS on brass in TiO\textsubscript{2} nanofluids was enhanced with the increase of SDBS concentration. When the amount of dispersant SDBS was more than a certain value, the corrosion resistance of brass would be reduced.

References
[1] U.S. Chio 1995 Asme Fed 66 99-105.
[2] Rashidi A, Amrollahi A, Lotfi R, Javaheryzadeh H. Rahimi H, & Rahimi A R and Jorsaraei A 2013 Mater. Res. Bull. 48 4438-4443.
[3] Krishnamurthy S, Bhattacharya A P, Phelan P E and Prasher R S 2006 Nano Lett. 6 419-23.
[4] Prasher R, Phelan P E and Bhattacharya P 2006 Nano Lett. 6 1529-1534.
[5] Haddad Z, Abid C, Oztop H F and Mataoui A 2014 Int. J. Therm. Sci. 76 168-189.
[6] Rashidi A M, Packnezhad M, Moshrefi-Torbati M and Walsh F C 2014 Microfluid. Nanofluid. 17 225-232.
[7] Yang L, Du K, Zhang X S and Cheng B 2011 Appl. Therm. Eng. 31 3643-3647.
[8] Xue-Min X U, Hong-Hua G E, Jia-Ni W U, He-li X U and Zuo-zhen L 2012 Corrosion & Protection
[9] Nagy E, Feczkó T and Koroknai B 2007 Chem. Eng. Sci. 62 7391-7398.
[10] Xin-jing M, Dong-chen J and Hong-hua G 2004 Chemistry World 8 473-474.
[11] Tavakoli H, Shahrahi T and Hosseini M G 2008 Mater. Chem. Phys. 109 281-286.

Acknowledgements
The authors acknowledge the financial support of the National Natural Science Foundation of China (51471104) and Science and Technology Commission of Shanghai Municipality (16dz0503302)