Oxidation and Electrochemical Behavior of Monolayer-Graphene-Coated Copper in Simulated Primary Water

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Received: 28 August 2015 / Revised: 1 December 2015 / Published online: 9 January 2016
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Abstract In high-temperature and high-pressure water, traditional anticorrosion approaches are not suitable to be used to protect structural materials from oxidation and corrosion. In this study, monolayer graphene was explored as a barrier to protect the materials from degradation. The oxidation and corrosion rate of the monolayer-graphene-coated copper is much lower than that of the bare copper, suggesting that the monolayer graphene can effectively protect the copper from oxidation and corrosion in the simulated primary water of pressurized water reactors.

KEY WORDS: Monolayer graphene; Oxidation behavior; Electrochemical behavior; Simulated primary water

1 Introduction

In high-temperature pressurized water, such as in the pressurized water reactors (PWR), oxide products play a crucial role in stress corrosion cracking of the key metallic components during service [1–3]. In addition, the heat transfer efficiency of the tubes used in fabricating steam generators can be decreased by the oxide films on their surfaces, which correspondingly decreases the efficiency of electricity generation of nuclear power plants. However, unfortunately, traditional anticorrosion approaches are not suitable to be applied to protect these materials from oxidation and corrosion as the traditional coatings are not stable in high-temperature (~ 290 to ~ 330 °C) and high-pressure (~ 15.5 MPa) water or as they are adverse in

controlling the water chemistry of the primary water and the secondary water.

Graphene, as the thinnest known material, has been widely studied across the world. Up to now, many researchers have proved that the graphene can act as an antioxidation and anticorrosion barrier under a variety of conditions where other materials would undergo rapid chemical reactions [4–12]. For instance, Kirkland et al. [4] found that graphene could effectively reduce the corrosion rate of nickel and copper when they were exposed to 0.1 mol/L NaCl solution. Chen et al. [8] found that the surfaces of Cu and Cu/Ni alloys were well protected by the coated graphene even when they were heated at 200 °C in air for up to 4 h.

Many properties of graphene, such as, can provide physical separation between substrate and reactants, chemically inert and stable in harsh environments, have determined it may have the potential to be a good antioxidation barrier in PWRs. What's more, our previous study has shown the perfect performance of the multilayer graphene to protect the nickel from oxidation in simulated primary water of PWRs [13]. Recently, the transferred monolayer graphene was also found that it could be a protective barrier for nickel-based 690 alloy in high-temperature and high-pressure water [14].

Available online at <http://link.springer.com/journal/40195>

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Though high-quality monolayer graphene is difficult to be synthesized on structural materials (e.g., stainless steels, nickel-based alloys and low alloy steels) used in PWRs, the technique to deposit high-quality monolayer graphene on pure copper is mature. As a result, monolayer-graphene-coated copper was used in this experiment. It is also important to note that copper is not used to fabricate any part of component in the primary loop of PWRs. The main purpose is to explore the usage of the monolayer graphene to protect the metallic materials from oxidation/corrosion in simulated primary water of PWRs.

2 Materials and Methods

Low-pressure chemical vapor deposition (LPCVD) was used to synthesize the monolayer graphene, and the brief process was: a copper foil with a thickness of 25 μm (Alfa Aesar, 99.8%) was annealed under a hydrogen flow at 1000 $^{\circ}\text{C}$ for 30 min, and then it was exposed to a mixture of hydrogen and methane at a total pressure of 50 Pa for another 30 min before it was cooled down to room temperature.

Then both the graphene-coated copper (G/Cu) sample and the bare copper (Cu) sample were immersed in simulated primary water of PWRs containing 1500 ppm (by weight) B as H_3BO_3 and 2.3 ppm (by weight) Li as $\text{LiOH}\cdot\text{H}_2\text{O}$. The immersion test was performed in a 1.4 L 316L-type autoclave at 300 $^{\circ}\text{C}$ for 250 h. Before elevating the temperature, the simulated primary water was deaerated by high pure nitrogen gas (99.99%) for 4 h at 70 $^{\circ}\text{C}$. The Cu and G/Cu samples were characterized by scanning electron microscopy (SEM, FEI XL30), Raman spectroscopy (Jobin Yvon HR800) before and after immersion experiment.

The electrochemical impedance spectroscopy (EIS) was performed in the same simulated primary water in a three-electrode cell by using 273A Potentiostat/Galvanostat (EG&G PAR) and 5210 lock-in amplifier, while the potentiodynamic polarization was performed in the same solution by using CHI660D. The working electrode was a Cu or G/Cu sample (tested area was $\sim 0.35\text{ cm}^2$), the counter electrode was a platinum foil with a surface area of $\sim 2\text{ cm}^2$, and the reference electrode was a saturated calomel electrode (SCE). Both the EIS and the potentiodynamic polarization were performed at room temperature. In order to get a stable open-circuit potential (E_{ocp}), the working electrode was immersed in the solution for 30 min before electrochemical measurement. The EIS tests were carried out over a frequency between 100 kHz to 10 mHz using a 10 mV amplitude of sinusoidal voltage variation around the E_{ocp} . The scanning rate of the potentiodynamic polarization tests was 0.5 mV/s.

3 Results and Discussion

Figure 1a shows the SEM image of the G/Cu sample. Wrinkles or edges of the graphene are apparent. The typical Raman spectrum of the graphene on Cu foil with the G band around 1580 cm^{-1} and the 2D band around 2700 cm^{-1} is shown in Fig. 1b. D band around 1350 cm^{-1} reveals the defects of the graphene cannot be found, suggesting that the graphene synthesized on the Cu foil is in high quality [15]. The ratio of integrated intensity of the G band to the 2D band ($I_{\text{G}}/I_{2\text{D}}$ ratio) is 0.45, indicating that monolayer graphene is synthesized. SEM image of Cu sample is shown in Fig. 1c, and the rolling indentions on it are evident. The growth process of the graphene on Cu is self-limited, that is, once the Cu foil is thoroughly covered by one layer of the graphene, the growth process will be stopped because of the very low C solubility in Cu and poor C saturation [16]. And as a result, it is very easy to get the monolayer-graphene-coated Cu foil by CVD.

Figure 2a, b shows the SEM images of the Cu and G/Cu samples after immersion experiment, respectively. Figure 2c, d is higher magnification SEM images of Fig. 2a, b, respectively. Large amount of oxides can be observed on the Cu sample, especially at the places with the rolling indentions. However, only a few oxides can be found at the locations where the graphene has cracks on the G/Cu sample. The cracks can provide the paths for the diffusion of the metallic ions (e.g., Cu^{2+} and Cu^{+}) from the Cu surface to the solution/graphene interface. Once the metallic ions reach the solution/graphene interface, they will react with O^{2-} or OH^{-} to form the oxides. However, evidently, no oxides can be found at the places where Cu substrate is covered by graphene with no cracks on the G/Cu sample, indicating that the monolayer graphene can act as a potential antioxidation barrier in the simulated primary water.

Raman spectrum of the monolayer graphene on G/Cu sample after immersion is shown in Fig. 3. The peak marked by D increases, while the peak marked by 2D decreases, indicating that the defects were introduced to the graphene during the immersion process. However, the monolayer graphene can act as a good barrier to protect the substrate from oxidation if it has no cracks as the oxide particles are only found at the cracks.

The anodic and cathodic polarization curves for the corrosion of Cu and G/Cu samples are shown in Fig. 4a. The E_{ocp} (open-circuit potential) of Cu and G/Cu are very different in some published articles, and some results are even in contrast with others. Raman *et al.* [7] found that the E_{ocp} of G/Cu was 40 mV more positive as compared to the bare Cu in 0.1 mol/L sodium chloride (NaCl) solution, and Prasai *et al.* [6] found the E_{ocp} of G/Cu was 25 mV higher

Fig. 1 SEM image of the G/Cu sample **a**, Raman spectrum of the graphene on the G/Cu sample **b** and SEM image of Cu sample **c**

Fig. 2 SEM images of the Cu sample **a** and the G/Cu sample **b** after immersion. **c** and **d** are higher magnification SEM images of **a** and **b**, respectively

than Cu in 0.1 mol/L Na₂SO₄ electrolyte. However, Kirkland *et al.* [4] found that the E_{ocp} of Cu was 150 mV higher than Cu in 0.1 mol/L NaCl solution. No matter whether the $E_{\text{ocp,G/Cu}}$ is higher than $E_{\text{ocp,Cu}}$ or not, the corrosion rate of the G/Cu is much lower than that of the bare Cu. So the E_{ocp} is not a precise parameter to claim the corrosion rate of Cu and G/Cu in these solutions even it is always the measure of corrosion susceptibility. In this research, the E_{ocp} of Cu sample is 51 mV, about 87 mV higher than that of the G/Cu sample, and this also does not mean that the Cu

sample has higher corrosion resistance as the corrosion current density (i_{corr}) of Cu sample ($i_{\text{corr,Cu}} = 1.4 \times 10^{-7}$ A/cm²) is about four times higher than that of G/Cu sample ($i_{\text{corr,G/Cu}} = 3.3 \times 10^{-8}$ A/cm²). Corrosion rate v_{corr} can be calculated from the equality $v_{\text{corr}} = i_{\text{corr}} \times M_{\text{Cu}} / (F \times n \times \rho)$, where M_{Cu} is the molecular mass for Cu, F is the Faraday's constant, n is the stoichiometric coefficient of the electron in the electrode reaction and ρ is the density of Cu. The v_{corr} of G/Cu is four times lower than that of Cu, suggesting that the monolayer graphene

Fig. 3 Raman spectrum of the monolayer graphene on the G/Cu sample after immersion

can significantly decrease the corrosion rate of Cu in the simulated primary water of PWR at room temperature.

The impedance ($|Z|$) plots of Cu and G/Cu samples are shown in Fig. 4b. When the frequency tends to be zero, the $|Z|$ tends to be Z_{real} (real impedance, a measure of the corrosion resistance). The impedance of G/Cu sample at the lowest frequency is about four times higher than that of the Cu sample, consistent to the relationship between the $i_{\text{corr, Cu}}$ and $i_{\text{corr, G/Cu}}$, again indicating that the monolayer graphene can protect the Cu from corrosion.

As in the previous articles [5, 7], $R(Q(R(CR)))$ electrical equivalent circuit was used to fit the impedance data, as shown in Fig. 5. R_{sol} represents the electrolyte resistance, C_{dl} and R_c represent the metal/electrolyte interface, constant phase element Q_f , and a pore resistance R_f represent the surface coating [7]. The values of different parameters associated with the electrical equivalent circuit are summarized in Table 1. The values of R_{sol} , Q_f , n , R_f and C_{dl} of

Fig. 5 Electrical equivalent circuit used to simulate the impedance data of Cu and G/Cu

Cu sample and G/Cu sample are not much different, while R_c of the G/Cu sample is about four times higher than that of the bare Cu. The corrosion resistance is the mathematical sum of R_f and R_c [7], so the corrosion resistance of G/Cu is higher than the bare Cu.

Another aspect to evaluate the coatings is the adhesion forces between the coatings and the substrate. The adhesion energy of the monolayer graphene to Cu is 0.75 J/m^2 obtained by using atomic force microscopy with a microsphere tip [17]. And the adhesion energy is about two times higher than the transferred monolayer graphene. According to our experiment, after 500 h immersion in the high-temperature and high-pressure water, the transferred monolayer graphene still stick to the 690TT alloy [14]. What's more, the monolayer has very high adhesive force as it has very high area–volume ratio, so the adhesion force between the graphene and Cu is enough.

Schematic diagrams (Fig. 6) are used to explain why the graphene can protect Cu in simulated primary water. The main reason is that the graphene can physically separate Cu and corrosive environment. For bare Cu (Fig. 6a), Cu atoms loose electrons to become Cu ions and dissolve to solution. These ions will react with O^{2-} or OH^- to form oxides or hydroxides. However, if the Cu is covered by monolayer graphene (Fig. 6b), the reaction will be stopped as Cu^{2+} , O^{2-} and OH^- ions cannot pass the monolayer graphene. By creating an airtight ‘balloon,’ Bunch et al.

Fig. 4 Polarization curves **a** and impedance plots **b** for the Cu and G/Cu samples in the simulated primary water of PWR

Table 1 Values of different parameters associated with the electrical equivalent circuit

Sample	R_{sol} ($\Omega \text{ cm}^2$)	Q_f (F/cm^2)	n	R_f ($\Omega \text{ cm}^2$)	C_{dl} (F/cm^2)	R_c ($\Omega \text{ cm}^2$)	Chi-squared
Cu	4736	2.17×10^{-6}	0.63	799	1.08×10^{-6}	4.06×10^5	2.44×10^{-4}
G/Cu	4623	1.61×10^{-6}	0.61	773.4	1.87×10^{-6}	1.67×10^6	6.29×10^{-4}

Fig. 6 Schematic diagrams used to explain why the graphene can protect Cu in simulated primary water: **a** bare Cu, **b** G/Cu

[18] have demonstrated that a monolayer graphene is impermeable to standard gases including helium. But, when the graphene has cracks, the cracks can provide the paths for the diffusion of metallic ions, O^{2-} and OH^- to form oxides. The second reason is that the graphene is chemically inert and is stable in high-temperature air [8] or under conditions where other substrates will undergo rapid chemical reactions [4, 5, 7]. After immersion in the high-temperature and high-pressure water for even 1000 h, multilayer graphene can still keep its own structure [13].

Even though the graphene can effectively protect the materials from corrosion, large-area and high-quality graphene is very difficult to be synthesized on the structural material (e.g., stainless steels and nickel-based alloys). Other approaches should be explored to coat the graphene on these materials.

4 Conclusions

The performance of the monolayer graphene as an antioxidation and anticorrosion barrier in the simulated primary water of PWR is studied by using the immersion experiment and the electrochemical measurement. No

oxide is found at the places coated by the monolayer graphene (with no cracks), indicating that it can protect the substrate from oxidation. The corrosion rate of the graphene-coated copper is four times lower than that of the bare copper, suggesting that the monolayer graphene can protect the substrate from corrosion. In conclusion, the monolayer graphene can be a potential barrier to protect the substrate from oxidation and corrosion in PWRs.

Acknowledgments This work was financially supported by the National Basic Research Program of China (No. 2011CB610502) and the National Natural Science Fund for Distinguished Young Scholars (No. 51025104).

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