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Improved alkaline hydrogen evolution performance of a Fe₇₈Si₉B₁₃ metallic glass electrocatalyst by ultrasonic vibrations

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ABSTRACT

The electrocatalytic performance of a $Fe_{78}Si_9B_{13}$ amorphous alloy toward alkaline hydrogen evolution reaction (HER) is enhanced by ultrasonic vibration (UV). The UV treatments slightly increase the crystallization enthalpy of the $Fe_{78}Si_9B_{13}$ amorphous alloy from 141.54 J/g to 145.32 J/g, meanwhile a large number of micro-cracks, -holes and -chips are generated on the surface of the amorphous alloy. The overpotentials of the amorphous alloy treated with ultrasonic energy of 5000 J is only 173 mV at 10 mA cm⁻² in 1.0 M KOH, which is reduced from 386 mV for the amorphous ribbon alloy at the same conditions. Moreover, the UV treated amorphous alloys also show better HER cycling performance comparing with those of the amorphous alloy without UV treatment. After 1000 CVs, it only needs 127 mV to reach the current density of 10 mA cm⁻² for the materials treated with 5000 J. After 1000 CVs cycling reaction, the UV treated amorphous alloy shows much enlarged specific area compared with that of the untreated amorphous alloy, which should be the reason for the improved cycling HER performance.

decade.

degrade several organic dyes such as methyl orange and methylene blue. Similarly, Duan [12] et al. reported that the Cu-based MGs with fine

particle size, high electrochemical active area, can efficiently and stably

oxidizes CO₂ to formic acid (HCOOH), ethanol (C₂H₆O) and other's

chemical raw materials. Especially, as catalysts of hydrogen evolution

reaction (HER). Ju [13] et al. and Hu [9] et al. separately reports the

excellent catalytic ability and stability of $Al_{80}Ni_6Co_3Mn_3Y_5Au_3and$ $Pd_{40}Ni_{10}Cu_{30}P_{20}$ MGs as HER catalysts. It is worth noting that their

catalytic activities are very close to that of commercial Pt/C. However,

the reported MGs with high HER catalytic activities usually contain

more or less noble metals, making them less promising materials for

large-scale industrial applications. Therefore, MGs without containing

precious metals are more and more studied as HER catalysts in the last

electron transfer ability and friendly environmental compatibility, Fe-

based MGs have becoming promising catalysts in the field of

As a result of low materials cost, suitable activation energy, good

1. Introduction

Metallic glasses (MGs), also known as amorphous alloys, have distinctive disordered atomic packing structures and metastable characteristics compared those with the well-ordered atomic packing structures in crystalline alloys. Because of their unique atomic structures, MGs have been explored to show many superior mechanical, magnetic and electrochemical properties in the past decades [1,2]. MGs have been widely studied as structural and functional materials due to their high yield strengths [3], superior elasticity [4], soft magnetic properties [5] and superior corrosion resistance [6], etc.

In recent years, MGs have also attracted more and more attentions in the catalysis field because of tunable chemical components [7], physical isotropy, chemical heterogeneity [8], high electrocatalytic activity and wonderful self-reconstruction ability [9] etc. Jia [10,11] et al. reported that the $Fe_{78}Si_9B_{13}$ MGs can serve as an efficient and reusable photo-degradation catalyst for improving the persulfate activation to

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Scheme 1. Preparation process of amorphous Fe78Si9B13 active glass alloy.

electrochemical catalysis [14–16]. Zhang [17] et al. summarized the excellent performance of most common Fe-based amorphous alloys in the field of catalytic degradation of dyes, in particular, $Fe_{78}(Si, B)_{22}$ MG exhibits lower activation energy and faster electron transfer speed, leading to more efficient dye degradation efficiency than that of the crystalline iron catalysts. Among them $Fe_{78}Si_9B_{13}$ MG can greatly photo-enhance the degradation of bright red 3B-A (BR3B-A) dye and shows excellent surface stability in the degradation of methyl blue (MB) by activated persulfate (PS), which show the excellent ability to catalyze degradation of dyes [18]. However, the best formers of Fe based MGs is usually limited by a narrow composition range [19]. Further improving the HER catalytic activities of Fe based MGs remains an issue.

High-frequency vibration can make MGs to form a large amount of free volume, thereby increasing its plastic deformation ability [20,21], furthermore, the free volume is created by the transition of atoms from loose atomic packing structure to close atomic packing structure, which means that the atoms of MGs may be in higher energy state [22], we assume that MGs with high energy atoms as "active glasses", and it is a reasonable prospect that the active glass may lead to excellent catalytic ability for HER. Traditional plastic processing technology easily causes crystallization of amorphous alloys. Ultrasonic beating forming (UBF) [23] and ultrasonic vibration (UV) [24] are new rapid forming methods for processing MGs, It is worth noting that the heat is transferred out at a very fast speed to avoid crystallization. Therefore, it is considered as an efficient, economical and stable way to product "active glass" for MGs without crystallization.

In the present work, a $Fe_{78}Si_9B_{13}$ MG was prepared by melt spinning followed by UV. The UV process not only generates a large number of nanoscale interfaces from fine cracks, holes and glass chips on the surface, but also increases the atomic energy of amorphous $Fe_{78}Si_9B_{13}$ alloy however without crystallization, leading to significantly improved catalytic performance and stability for alkaline HER. This study may provide new ideas for the development of low-cost active glass catalysts for HER, and the materials preparation method is also suitable for largescale applications.

2. Materials and methods

Scheme 1 shows the preparation process of materials. Firstly, the $Fe_{78}Si_9B_{13}$ amorphous alloy ribbons were prepared by melt spinning in a high-purity argon (99.999%) atmosphere. Secondly, the ribbons with width of 6 cm and thickness of 20 μ m were cut into circle pieces with a diameter of $\Phi = 10$ mm by a punching machine. Thirdly, 5 pieces of the punched circles were put into a Branson 2000X Ultrasonic Welding Machine for ultrasonic vibration (UV) process. The experimental parameters of UV are as follows: welding pressure of 200 KPa, trigger pressure of 200 N, vibration amplitude of 80%, holding time of 12 s, and the ultrasonic energy applied to the $Fe_{78}Si_9B_{13}$ amorphous alloys are 50 J, 500J and 5000J, which are marked as UV-50J, UV-500J and UV-5000J, respectively.

Electrochemical measurements were carried out at room temperature with CHI600E electrochemical workstation (CH Instruments Ins),



Fig. 1. a) XRD patterns and b) DSC curves obtained at heating rate of 10 K/m in a high-purity argon (Ar@99.999%) atmosphere of the amorphous Fe₇₈Si₉B₁₃ alloys and UV-5000J sample.



Fig. 2. XPS curves of the amorphous $Fe_{78}Si_9B_{13}$ alloy and UV-5000J sample a) Fe *2p*, b) Si *2p*, c) B *1s*.

using a traditional three-electrode system. For the measurements, glassy carbon electrode with catalyst was used as working electrode, a saturated Ag/AgCl electrode and graphite rod were employed as the reference and counter electrodes, respectively. All the measured potentials have been calibrated with respect to RHE. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were studied at scan interval from -0.78 V to 0.02 V (RHE) with the scan rate of 10 and 100 mV/s, in 1.0 M KOH electrolyte, respectively. Tafel plots were derived from the LSV at

5 mV/s curves. Electrochemical impedance spectroscopy (EIS) was obtained with the parameters of frequencies ranging from 100 000 Hz–0.1 Hz at the potential of overpotentials at 10 mA cm⁻².

Microstructures and chemical compositions of the MG ribbons before and after UV and HER reaction were studied at a field emission scanning electron microscope (FE-SEM, ZEISS UL TRA 55) with an energy dispersive X-ray spectrometer (EDS). The phase structures were conducted at X-ray diffraction (XRD, Ultima IV). Atomic valence of MGs ribbons was performed at X-ray photoelectron spectroscopy taking C 1s as a reference (XPS, Thermo Scientific Escalab 250Xi).

3. Results and discussion

3.1. Phase structure and crystallization behavior

Fig. 1a shows the XRD patterns of the amorphous $Fe_{78}Si_9B_{13}$ alloys before and after UV treatments. Even at the highest ultrasonic energy of 5000J, the amorphous alloy does not crystallize. We believe that preserving the atomic packing structure of amorphous alloys is an advantage for catalytic behavior based on our previous experiences on study of hydrogenation properties of amorphous and crystalline alloys [25–27]. Fig. 1b shows the crystallization behavior of amorphous $Fe_{78}Si_9B_{13}$ alloy and the UV-5000J sample. It can be clearly seen that the enthalpy change of crystallization ($\triangle H_C$) for the amorphous $Fe_{78}Si_9B_{13}$ alloy is 141.54 J/g, which is close to the results reported by Wei et al. [28]. After UV treatment with energy of 5000J, $\triangle H_C$ is increased to 145.32 J/g because the high-energy atomic structure caused by free volume will release more energy during the crystallization process [29]. Moreover, it also illustrates that the UV treatment changes the atomic structure of the amorphous alloy, which one changes from loose to compact.

To understand the surface chemical state of the $Fe_{78}Si_9B_{13}$ amorphous alloy after UV process, XPS experiments were carried out as shown in Fig. 2. The XPS curves are corrected by C1s (284.6 eV). As shown in Fig. 2a–c, the Fe *2p* (Fe0 at 706.5eV & 719.1eV, Fe2+ at 710.4eV, Fe3+ at 723.9eV), Si *2p* (Si0 at 99.0eV, Si2+ at 101.9eV) and B *1s* (B⁰ at 187.4eV, B^{X+} at 191.4eV) curves [30,31], there is no obvious difference in the chemical state for the ribbons alloys before and after UV, indicating that UV process does not change the surface chemical state for the amorphous alloys. It is worth noting that oxygen element of all sample exists as Fe–O bond (FeO at 710.4 eV& Fe₂O₃ at 723.9eV) and Si–O bond (SiOx at 101.9 eV) [32].

Based on the above XRD, DSC and XPS results, it can be concluded that there are no side reactions and impurities introduced in the UV process, moreover, the most important thing is that the increase of crystallization enthalpy indicates that the conversion of atomic packing structure of amorphous alloys from loose into compact, which might be beneficial for the catalytic activity.

3.2. Microstructure characterizations

Microstructures of the melt-spun $Fe_{78}Si_9B_{13}$ alloy before and after UV treatments are shown in Fig. 3. The surface of the melt-spun alloy is very flat, but it is fragmented upon high frequency vibrations as shown in Fig. 3b–d, which cause abundant cracks and glass chip. Fig. 3e, after UV treatments, more details of the crack and glass chip, it shows that cracks are staggered in the MGs. Fig. 3f shows the EDS mapping of a glass chip. It reveals that glass chip peeled off from the sample with the largest vibration energy, contains a small amount of oxygen, which may be a trace oxide film formed during the spinning process or ultrasonic treatment.

3.3. HER catalytic activity

LSV curves, Tafel slopes, EIS curves and cyclic stability were used to evaluate the HER catalytic effect of the amorphous $Fe_{78}Si_9B_{13}$ alloy before and after UV treatments (Fig. 4). As shown in Fig. 4a, the onset



Fig. 3. SEM images of the Fe₇₈Si₉B₁₃ amorphous alloy upon UV treatments: a) Fe₇₈Si₉B₁₃ amorphous alloy, b) UV-50J, c) UV-500J, d) UV-5000J. e) EDS mapping of the glass chips of the UV-5000J sample. f) showing micro-cracks of the UV-5000J sample.

potential of the amorphous $Fe_{78}Si_9B_{13}$ ribbons has gradually reduced as the UV energy increases. Besides, at a current density of 10 mA cm⁻², the UV-50J, UV-500J and UV-5000J samples generate overvoltages of 300 mV, 240 mV and 173 mV, respectively, much smaller than the value for the $Fe_{78}Si_9B_{13}$ alloy of 386 mV. These results indicate that UV treatment can improve the HER catalytic activity of Fe-based MGs in alkaline media. It is worth noting that, different from Tafel slope, overpotential is a thermodynamic tendency, reflecting degree of difficulty of the catalyst at the beginning of the catalysis [33]. When the catalysts exhibit slower kinetics, the thermodynamic tendency of HER, which means that the UV-5000J sample exhibits the best thermodynamic tendency (overpotential of 173 mV at 10 mA cm⁻²).

Tafel slope is related to the kinetics of HER, which can be obtained from the LSV curves based on the Tafel equation ($\eta = a+blogj$) where η , j and b are the overpotential, current density and Tafel slope, respectively. Amorphous Fe₇₈Si₉B₁₃ catalysts show Tafel slopes (Fig. 4b) of 152 mV/dec, 154 mV/dec, 156 mV/dec and 169 mV/dec for the original ribbon, UV-50J, UV-50J and UV-5000J samples, respectively, which indicate that the HER rate-limiting steps of the amorphous Fe₇₈Si₉B₁₃ catalysts (over 120 mV/dec) are typical Volmer reaction process and showing a slower reaction kinetics [34]. After UV treatment, as the free volume increases, the average electron free path of the material decreases, which in turn reduces the conductivity, resulting in a slight increase in the Tafel slope, because of that the conductivity of the catalyst affects its Tafel slope. Furthermore, a poor conductivity often means a slow electron transfer rate, which shows a slow reaction kinetics.

EIS curves can directly evaluate the electrode kinetics of the MGs in the reaction, meantime the smaller value of the polarization resistance means faster electronic transport process and Faradaic behavior in HER kinetics. It can be clearly seen that polarization resistance value is gradually improving with the increase of ultrasound capability from Fig. 4c. Polarization resistance has close relation with defect structure.

Classical electronic theory believes that resistance is the result of collision between electrons and defective structures. According to the conductivity formula $\gamma = ne^2 \lambda / \nu m_e$ (γ is the conductivity, n is the average density of free electrons, *e* is the amount of electrons, λ is the average free path of electrons, ν is the average speed of electrons and m_e is the average mass of electrons), it can be seen that the conductivity is



Fig. 4. a) LSV curves, b) Tafel slopes and c) EIS curves of the Fe₇₈Si₉B₁₃ ribbons before and after UV; d) LSV curves, e) Tafel slopes and f) EIS curves of the Fe₇₈Si₉B₁₃ alloy and UV-5000J sample before and after long-term CV.

proportional to the average free path of electrons; Particularly, the defect structure will reduce the average free path of the electrons of the material, resulting in a decrease in conductivity [35]. Similarly, ultrasonic vibration treatment will not only destroy the Fe–Si–B MGs surface and produce a large number of surface defect structures, but also introduce a large amount of free volume inside the material, which we call its internal defect structure. Moreover the increase of ultrasonic energy will cause more defective structures, which means that the polarization resistance of the material will also increase, so the polarization resistance of Fe₇₈Si₉B₁₃ MG and ultrasonic energy show a positive correlation.

To further understand the polarization resistance, an equivalent circuit model is established as shown in the insert of Fig. 4c, where R_S is the resistance of alkaline electrolyte and R_{ct} is the resistance related to transfer charge. The obtained R_s and R_{ct} for the materials are show in Table 1. The R_S values (0.94, 0.87, 0.84, 0.90, 0.61 and 0.91 Ω cm²) of

Table 1

Fitting parameters for EIS, η at 10 mA cm⁻² and tafel slope data of the amorphous Fe₇₈Si₉B₁₃ alloys before and after UV and CV.

	R _s (ohm cm ²)	R _{ct} (ohm cm²)	η (mV)at 10 mA/cm ²	Tafel slope (mV/dec)
ribbon	0.94	2.46	386	152
ribbon 1000CV	0.87	19.76	334	164
UV-50J	0.84	2.08	300	154
UV-500J	0.90	10.36	240	156
UV-5000J	0.61	22.80	173	169
UV-5000J 1000CV	0.91	63.31	127	195



Fig. 5. a) The long-term durability tests of the original ribbons (η at 386 mV) and UV-5000J sample (η at 173 mV) alloys; b) XRD patterns of the original ribbons and UV-5000J sample before and after long-term stability test.

all catalysts are very close, interpreting that the electrolyte resistance maintained a relatively stable value in HER process. On the other hand, the R_{ct} related to transfer charge obviously increases from 2.46 Ω cm² to 22.80 Ω cm² upon UV treatments, which should be due to the numerous micro cracks, holes and chips generated on the surface of the amorphous alloy by UV (Fig. 3). Although the electron conductivity of the ribbons has decreased after UV treatment and long-term CV test, the decline trend is not so large. Even after 1000CV test, the sample of UV-5000J has a resistance of only 63.31 Ω cm², which show a small polarization resistance.

Fig. 4d shows the LSV curves of all amorphous $Fe_{78}Si_9B_{13}$ alloys before and after 1000 CVs. It can be find that the overpotentials of both $Fe_{78}Si_9B_{13}$ ribbons (334 mV at 10 mA cm⁻²) and UV-5000J sample (127 mV at 10 mA cm⁻²) have reduced after 1000 CV test, which should be owing to the unique self-reconstruction ability of MGs [36]. Particularly, the self-reconstruction behavior and chemical reaction not only have further damaged the alloy surface, but also produced some poorly conductive oxides or hydroxides on the alloy surface, which lead to the increase of resistance (Fig. 4f) and Tafel slopes (Fig. 4e) after cycling stability test.

3.4. HER cycling performance

Fig. 5a shows that the long-term stability of the original ribbon and UV-5000J sample. After 50 h continuous reaction, although the catalytic performance of both alloys has decreased, the UV-5000J sample has significantly higher HER catalytic activity than the original ribbon, interpreting that high-energy atomic structure is beneficial to improve the cycle durability of the catalyst.

According to the huge difference of the overpotentials (Fig. 4d) and cycling performance before and after the Long-term CV test, it can be concluded that the main factor for HER catalytic behavior is the highenergy atomic structure obtained by UV because of that all the initial interfaces containing of micro-cracks, -holes and -chips on the surface gradually disappear as the reaction proceeds. Therefore, it is supposed that the high-energy atomic structure induced by UV treatments should be the key for improving the excellent HER behavior.

To further study the excellent HER cycling performance of the UV-treated amorphous alloys, morphology evolution of original ribbon and the UV-5000J sample during the after 1000 CVs are compared in Fig. 6. Fig. 6a–f shows the EDS mapping of UV-5000J sample after 1000CV cycles. According to report of Liu [37] et al., the reaction of Fe atoms in Fe-based MGs in alkaline media: FeH (ads) \rightarrow Fe \rightarrow FeOH (ads) \rightarrow Fe(OH)₂/FeO \rightarrow FeOOH, and the oxygen element has enriched in the flaky nanostructures as shown in EDS mapping, therefore, based on the above all information, it can be concluded that flaky nanostructures are

nano-flakes FeOOH/Fe(OH)₃. It is obvious that the two alloys show very different morphologies after 1000CVs as shown in Fig. 6g and h, the original ribbon forms some regular nano-rod with diameter of about 300 nm, but the UV-5000J sample shows the irregularly distributed nano-flake of FeOOH/Fe(OH)₃ with a size of about 100 nm. The formation of nano-rods may be the result of amorphous alloys' self-reconstruction behavior. On the other hand, the high-energy atomic structure of UV-5000J sample is inclined to generate irregular nano-flake FeOOH/Fe(OH)₃, which owns larger specific area to contribute to improve the HER catalytic activity [38].

Although both HER cycled alloys are amorphous as shown in the XRD patterns (Fig. 5b), more information of reaction path before and after HER cycling are studied by XPS (Fig. 7a–c). All the XPS curves have been corrected by C1s (284.6 eV). After 1000 CV, the Fe⁰ peaks at 706.5eV & 719.1eV have disappeared, which indicates that Fe⁰ is consumed as the main active substance in HER. In addition, due to the self-reconstruction behavior caused by Fe–Fe, Fe–Si and Fe–B bonds reduction, Si elements (Si⁰ at 99.0eV, Si²⁺ at 101.9eV) and B elements (B⁰ at 187.4.9eV and B^{X+} at 191.4eV) all have been dealloyed in the electrolyte as ionic or oxide form.

4. Conclusion

In summary, HER performance of a Fe78Si9B13 amorphous alloy was improved by ultrasonic vibration (UV). UV treatments slightly increase the crystallization enthalpy of the $Fe_{78}Si_9B_{13}$ amorphous alloy from 141.54 J/g to 145.32 J/g, meanwhile a large number of micro cracks, holes and chips were generated on the surface of the amorphous alloy. The UV treated amorphous alloys exhibits the significantly improved HER catalytic ability. The overpotentials of the amorphous alloy treated with ultrasonic energy of 5000 J is only 173 mV at 10 mA cm $^{-2}$ in 1.0 M KOH, which was reduced from 386 mV for the amorphous ribbon alloy at the same conditions. Moreover, the UV treated amorphous alloys also show good HER cycling performance comparing with those of the untreated amorphous alloy. After 1000 CVs, there are abundant nanoflakes FeOOH/Fe(OH)3 generated on the surface of the UV treated amorphous alloy, showing much enlarged specific area compared with that of the nano-rods FeOOH/Fe(OH)3 on the surface of the amorphous Fe₇₈Si₉B₁₃ alloy, which should be the reason for the improved HER performance. This work shows that UV is a low-cost and effective method for improving the HER catalytic and cycling performances of Febased amorphous alloys.

CRediT authorship contribution statement

Kaiyao Wu: Investigation, Methodology, Writing - original draft.



Fig. 6. a-f) are the EDS mapping for Fe, Si, O and B, respectively; SEM images of the g) original ribbons and h) UV-5000J sample before and after 1000CVs.



Fig. 7. XPS curves of the amorphous $Fe_{78}Si_9B_{13}$ alloy and UV-5000J sample before and after1000CV: a) Fe 2p, b) Si 2p, c) B 1s.

Yuying Meng: Formal analysis, Writing - review & editing. Xin Li: Validation. Jiang Ma: Validation, Resources. Peng Zhang: Validation. Wei Li: Project administration. Lishan Huo: Validation, Resources. Huai-Jun Lin: Conceptualization, Funding acquisition, Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare no conflict of interest.

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