Advanced Laser Science Research Section

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1. Introduction

We use our knowledge and skills on laser science to fabricate the functional materials and probe the associated dynamics without perturbing the various processes. This year we have developed two different techniques: The first one is to fabricate Ni electrodes with enhanced performance for hydrogen evolution reaction (HER) and the second one is to fabricate high quality holes/lines for various purposes including the micro/nano-structuring of electrodes.

2. Efficient hydrogen evolution reaction with Ni electrodes textured by nanosecond laser pulses

Efficient production and use of hydrogen gas is one of the important means for renewable energy production. Water electrolysis using renewable energy is a practical and cost-effective way to produce hydrogen gas. In particular, alkaline water electrolysis (AWE) has a certain advantage that non-noble metals such as Ni, Fe, or their alloys can be used for electrodes and catalysts. Among others Ni has a very nice resistance against corrosion for AWE.

To attain the high efficiency of hydrogen evolution reaction (HER) through AWE texturing the surface of the electrode or the catalyst layer is one way, where the purpose of texturing is to enlarge the electrochemical surface area (ECSA) without/with the additional functionalization of the surface. Several recent works report the texturing of electrode surface by femtosecond laser with improved electrochemical performance. The main drawback of the use of femtosecond laser texturing is its cost and long processing time. A nanosecond laser system is much lower than that of a femtosecond laser system, and if nanosecond laser texturing of electrodes works well, it can be a practical alternative to fabricate the efficient electrode. To our knowledge there are no studies on nanosecond laser texturing of electrodes for efficient HER.

The purpose of this work is to perform nanosecond laser texturing of Ni electrodes under the different conditions, and study their electrochemical performance.

We employ a nanosecond MOPA fiber laser at the wavelength of 1064 nm and a nanosecond DPSS laser at the wavelength of 355 nm to texture the Ni substrates. Hereafter we call them near-infrared (NIR) and ultraviolet (UV) lasers, respectively. We texture the Ni substrates by nanosecond NIR and UV lasers in three different ambient gases, air, N_2, and Ar at 2 atm, and study their electrochemical performance for HER by taking the polarization curves and compare them with that of polished Ni electrode (roughness R_a~5 nm).

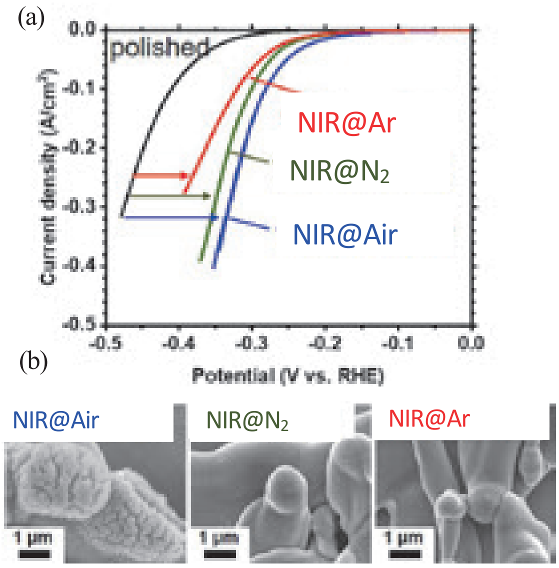


Fig. 1 (a) Polarization curves for HER by Ni electrodes textured with NIR (1064 nm) laser in air, N_2, and Ar gas. (b) SEM images of the NIR laser textured Ni electrodes.

Figure 1(a) shows the IR-corrected polarization curves for the NIR laser-textured electrodes in different ambient gases. We notice that the NIR@Air electrode shows the smallest overpotential. The main reason for this can be understood from the corresponding SEM images shown in Fig. 1(b), where the NIR@Air exhibit the most complicated cauliflower-like micro/nano-structures arising from the oxidation and hence volume expansion of the micro structures to result in cracks. Figure 2(a) shows the similar results for the Ni electrodes textured by UV laser. Different from the results for NIR laser texturing, UV@N_2 and UV@Ar show the smallest overpotential. Again, the main reason for this can be understood by the inspection of the corresponding SEM images (Fig. 2(b)): The UV@N_2 and UV@Ar electrodes exhibit very fine micro/nano-structures which enhances the ECSA by more than several tens of

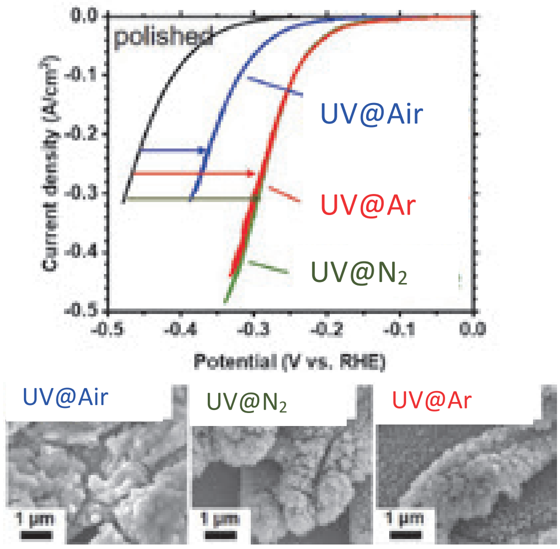


Fig. 2 (a) Polarization curves for HER by Ni electrodes textured with UV (355 nm) laser in air, N_2, and Ar gas. (b) SEM images of the NIR laser textured Ni electrodes.

times. The SEM image of the UV@Air electrode shows less micro/nano structures because the volume expansion associated with oxidation collapses the very fine structures to result in the reduced ECSA compared with those of the UV@N_2 and UV@Ar electrodes. We have also tested the durability of the fabricated Ni electrodes to find that the electrode textured by UV laser is most durable (Fig. 3).

3. Fabrication of depth-controlled high quality holes and lines on a metal substrate by picosecond laser pulses

To add some functions through materials processing is one of the important technologies in materials science. In particular, laser processing is a simple technique that is applicable in both dry and wet environments. The underlying mechanism of laser processing is of course laser ablation. As well known, the use of ultrafast lasers has a clear advantage to reduce the thermal effect. However, this holds only for the single shot process, and if the hole/line is fabricated on a metal substrate by multiple ultrafast laser pulses, the formation of ablation rims is inevitable even with ultrafast laser pulses.

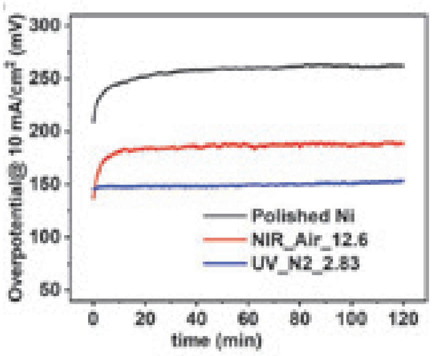
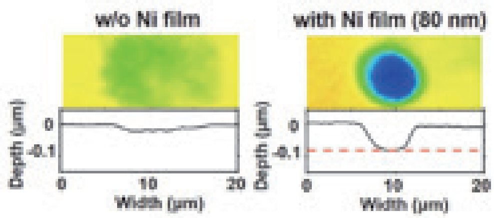


Fig. 3 Chronopotentiometric curves for the HER at the current density of -10 mA/cm^2.



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sponding cross-sectional view of the fabricated holes on the Ni substrates (a) without and (b) with Ni film (thickness 80 nm)

Based on the above thoughts we propose a simple idea to use a metal substrate with a thin metal film rather than a bare metal substrate to fabricate high quality holes/lines. Because the interface between the metal film and metal substrate is not metallically bonded, the metal film may be selectively blown out by the single laser pulse at a much lower laser fluence than that in the case of a bare metal substrate. As a result the metal substrate remains intact to show a flat metal surface with a nearly vertical sidewall.

We use mechanically polished Ni substrates with and without 80 nm Ni films as targets to fabricate holes and lines by picosecond laser pulses at 532 nm. Figure 4 shows that we can fabricate a high quality hole on the Ni substrate with a Ni film. Fabrication of high quality lines is much more challenging, since it requires multiple irradiation of laser pulses to form a line, and every single laser pulse can produce a very small thermal effect to deteriorate the quality of lines. Nevertheless, we are able to fabricate high quality limes only if we choose the appropriate laser fluence to minimize the thermal effects, as shown in Fig. 5. It is very interesting to point out that the slope of the sidewall of the line fabricated on a Ni substrate with a Ni film is nearly vertical with an extremely flat bottom, as shown in the right panel of Fig. 5.

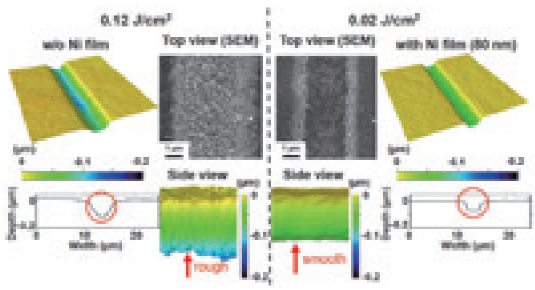

Fig. 5 False-colored morphologies and corresponding cross-sectional view of the fabricated lines on the Ni substrates (a) without and (b) with Ni film (thickness 80 nm)

Financial Support

1. Grant-in-Aid for Scientific Research

中嶋隆，基盤研究(B)，電極表面のガス種依存濡れ性制御による電解効率の飛躍的向上

2. Others

中嶋隆，（公財）市村清新技術財団，水素社会の実現に向けた高性能光学式水素センサーの開発

中嶋隆，新エネルギー・産業技術総合開発機構，燃料電池等利用の飛躍的拡大に向けた共通課題解決型産学官連携研究開発事業／水素利用等高度化先端技術開発／常温水電解の実用化基盤研究プラットフォームの構築

Publications

K. Sota, K. Ando, H. Zen, T. Kii, H. Ohgaki, T. Nakajima, Morphological study of depth-controlled high quality holes and lines fabricated on a metal substrate with a thin metal film by picosecond laser pulses, Optics and Laser Technology, 175, 110853, 2024

K. Sota, S. Mondal, K. Ando, Y. Uchimoto, T. Nakajima, Nanosecond laser texturing of Ni electrodes as a high-speed and cost-effective technique for efficient hydrogen evolution reaction, International Journal of Hydrogen Energy, 93, 1218-1226, 2024