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Layer reduction method fabricating Pd-coated Ni foams as high-performance ethanol electrode for anion-exchange membrane fuel cells

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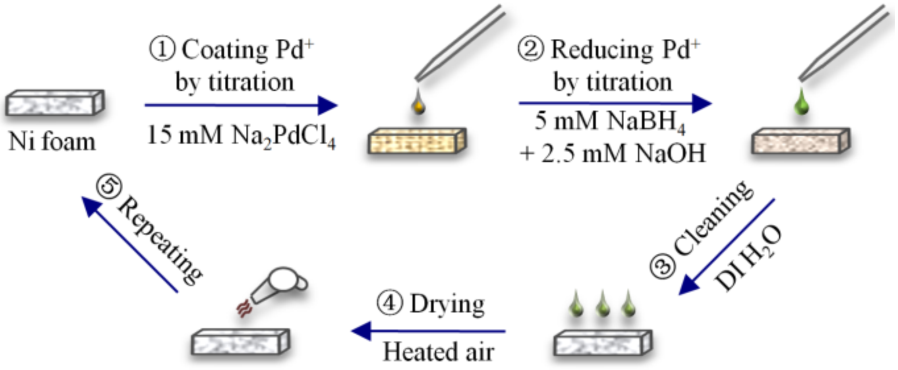

Fig. S1 Schematic illustration for preparing layer-reduced Pd/Ni foam electrode

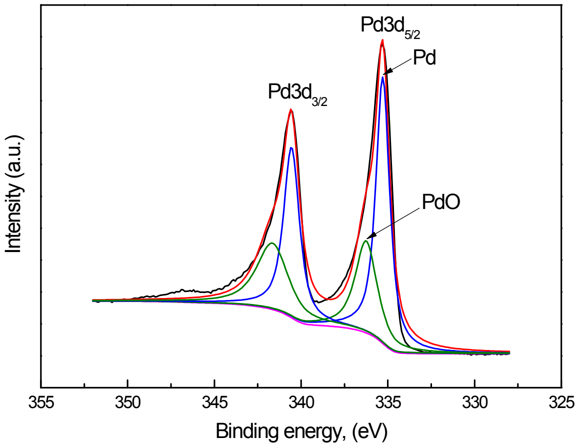

Fig. S2 Pd3d XPS spectrum of layer-reduced Pd/Ni foam electrode

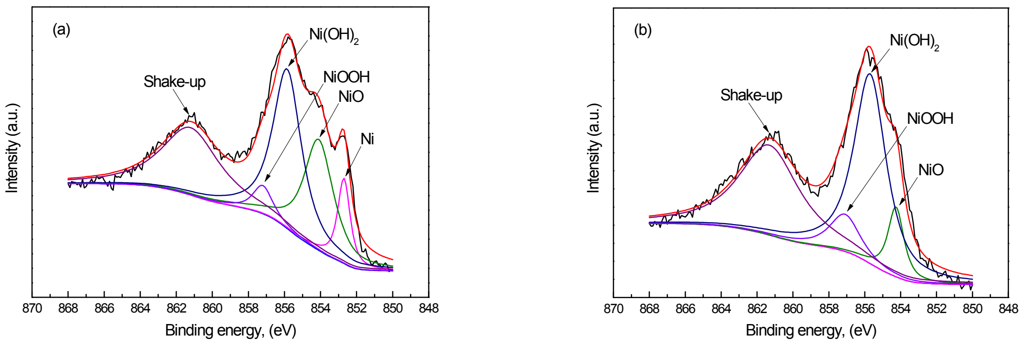

Fig. S3 Ni2p XPS spectra of (a) Ni foam and (b) layer-reduced Pd/Ni foam

Table S1 XPS area ratios of chemical states of Pd species

Sample	Area ratio (%)	
	Pd	PdO
Layer-reduced Pd/Ni foam	60.85	39.15

Table S2 XPS area ratios of chemical states of Ni species

Sample	Area ratio (%)			
	Ni	NiO	Ni(OH)$_2$	NiOOH
Ni foam	11.33	34.58	48.21	5.88
Layer-reduced Pd/Ni foam	0	13.36	73.16	13.48

The Pd3d XPS and Ni2p XPS spectra are respectively shown in Fig. S2 and Fig. S3. In Fig. S2, the Pd3d spectrum consists of a high-energy peak (Pd3d$_{3/2}$) at 340.5 eV and a low-energy peak (Pd3d$_{5/2}$) at 335.3 eV. The spectrum can be deconvoluted into two doublets at 335.3 and 336.2 eV, corresponding to metallic Pd and PdO, respectively [S1]. The XPS area ratios of various chemical states of Pd species (see Table S1) can be obtained by integrating the corresponding peaks shown in Fig. S2. It can be found that the Pd coated on the surface of the layer-reduced Pd/Ni foam mainly exists in its metallic state. In Fig. S3, the Ni2p spectra display two peaks i.e., a high-energy satellite peak and a low-energy main peak [S2, S3]. Considering the shake-up peak, the Ni2p spectrum can be deconvoluted into four doublets at 852.7, 854.1, 855.8 and 857.2 eV for Ni foam, and 852.7, 854.2, 855.7 and 857.1 eV for layer-reduced Pd/Ni foam, corresponding to metallic Ni, NiO, $Ni(OH)_2$ and NiOOH, respectively. The XPS area ratios of various chemical states of Ni species can be achieved by integrating the peaks shown in Fig. S3. The detailed ratios for both the layer-reduced Pd/Ni foam electrode and the treated Ni foam can be found in Table S2. It can be observed that the contents of metallic Ni and NiO on the surface of layer-reduced Pd/Ni foam electrode decrease as compared with that in the pristine Ni foam. Conversely, the contents of nickel hydroxides, $Ni(OH)_2$ and NiOOH increase. The possible reasons for the changed ratio of various Ni species in two samples are as follows. On one hand, it can be ascribed to the species chemical reactions, i.e., the surface metallic Ni was completely oxidized to nickel oxide in the heated air [S4], while partial nickel oxide reacts with water from the precursor solution to generate the nickel hydroxides [S5]. On the other hand, it can be attributed to the distribution of Ni species, i.e., the nickel hydroxides cover the surface of the layer-reduced Pd/Ni foam, which is confirmed by comparing the XPS spectra, however, the detecting depth of XPS is typically within top 12 nm of the material surface being analyzed, and this means the presence of the Pd thin film coated onto the surface of the Ni foam blocks the detecting signal to go deep into the skeleton of Ni foam, thereby leading to the reduced ratio of the metallic Ni and NiO.

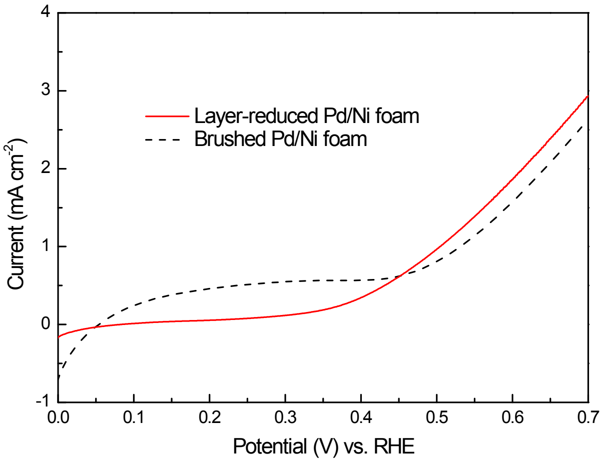

Fig. S4 Specific activity of the EOR on different electrodes in 1.0 M ethanol and 1.0 M KOH aqueous solution at a scan rate of 50 mV s^{-1}

The specific activity (i.e., the current density normalized by ECSA) of the EOR on different electrodes are compared. It is found that the specific activity of the EOR on layer-reduced Pd/Ni foam electrode is also higher than that on brushed Pd/Ni foam electrode, and this can be attributed the concurrent promotion effect from nickel hydroxides on the surface of the layer-reduced Pd/Ni foam. At a given a potential (e.g. 0.6 V), the specific activity of the EOR on layer-reduced Pd/Ni foam electrode is 1.87 mA cm^{-2}, 1.18 times of that on brushed Pd/Ni foam electrode. According to Fig. 5, the current at 0.6 V on layer-reduced Pd/Ni foam electrode is 1.86 times of that on brushed Pd/Ni foam electrode, it is concluded that the performance improvement in layer-reduced Pd/Ni foam electrode is mainly ascribed to the preceding great increased ECSA. In addition, the concurrent promoting effect from the nickel hydroxides also contributes to the performance improvement.

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