



# Simple anodization of home-made screen-printed carbon electrodes makes significant activity enhancement for hydrogen evolution: the synergistic effect of surface functional groups, defect sites, and hydrophilicity



Xiangheng Niu<sup>a,\*</sup>, Libo Shi<sup>b</sup>, Xin Li<sup>a</sup>, Jianming Pan<sup>a</sup>, Runxin Gu<sup>a</sup>, Hongli Zhao<sup>b</sup>, Fengxian Qiu<sup>a</sup>, Yongsheng Yan<sup>a</sup>, Minbo Lan<sup>b,\*</sup>

<sup>a</sup> Institute of Green Chemistry and Chemical Technology, School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China

<sup>b</sup> Shanghai Key Laboratory of Functional Materials Chemistry, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China

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## ABSTRACT

Undoubtedly, electrocatalyzing the hydrogen evolution reaction (HER) is now becoming the subject of extensive studies due to its crucial role in harvesting clean energy. In general, bare screen-printed carbon electrodes (SPCEs) have negligible ability to catalyze the HER due to the lack of effective sites. Here we find that: 1) a facile anodization treatment can improve the electrocatalytic activity of home-made SPCEs with apparently reduced overpotential and increased current density for the HER; 2) the activity enhancement of SPCEs is highly dependent on anodization conditions including electrolyte, treatment time, and anodization potential; 3) the introduction of negatively charged oxygen-containing functional groups during anodization, together with the increased defect sites and hydrophilicity on electrode surface, leads to the promoted activity of anodized SPCEs synergistically. Similar phenomena are also found in other carbon-based electrodes including glassy carbon electrode and carbon nanotube-modified electrode. These findings reported in this work are expected to guide the future design of advanced electrode systems for efficient hydrogen evolution.

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## 1. Introduction

Hydrogen is broadly considered as the future substitute for traditional fossil fuels due to its high energy density and environmentally friendly quality [1]. Harvest of hydrogen via water electrolysis has become a research hotspot for sustainable energy storage in recent years [2,3]. In the past few years, a lot of low-cost Pt-free metal electrocatalysts have been explored to promote the hydrogen evolution reaction (HER) [4–13]. Compared to metal-based materials, metal-free electrocatalysts seem to be more attractive for the HER [14–17], primarily because the former are prone to dissolve under practical operation conditions. Although the laboratory-measured performance of some of these advanced electrocatalysts has been much closed to that of commercial Pt/C, practical production of the green fuel with low

electrode cost and high current efficiency is still a desired goal for electrochemical energy.

Screen-printed carbon electrodes (SPCEs) are widely used as a substitute for glassy carbon electrodes (GCEs) thanks to their flexibility, robustness, and low-cost fabrication. Similar to bare GCEs, unmodified SPCEs have no noticeable activity for the HER, because the relatively smooth SPCE surface exposes very few active sites for heterogeneous electrocatalysis [18]. Fortunately, some processes including mechanical polishing [19,20], laser exposure [21], thermal treatment [20,22], plasma treatment [23,24], and electrochemical anodization [25–27] are able to change the inert properties of these carbon-based materials. Among these processes, electrochemical treatment is a convenient yet efficient method to acquire improved performance, with no requirement for fussy operations and advanced instruments. In previous studies, Zhao and co-workers found that the anodization treatment of GCEs could produce a negatively charged and densely compact oxide film on electrode surface [26]. Zen's group demonstrated that electrochemically anodized SPCEs were able to separate the peaks

\* Corresponding authors.

E-mail addresses: [niuxiangheng@126.com](mailto:niuxiangheng@126.com) (X. Niu), [minbolan@ecust.edu.cn](mailto:minbolan@ecust.edu.cn) (M. Lan).

of ascorbic acid, dopamine, and uric acid more remarkably compared to untreated SPCEs [28]. The same group also verified that treated SPCEs were able to promote the direct electron transfer of bio-enzymes immobilized on electrodes [29] and improve the adsorption and oxidation of polyaromatic hydrocarbons [30]. All of the above effects are considered to be much related to the surface chemistry changes (surface groups, defects, electrostatics, etc.) of electrodes before and after anodization. On the other hand, previous studies have demonstrated that the surface chemistry characters of electrodes have significant impacts on various electrocatalytic reactions including hydrogen evolution [14,17,31–33]. On the basis of these previous findings, a simple anodization process applied on carbon-based electrodes, supposedly, brings some interesting effects on the activity for the HER. In addition, a few issues underlying the hypothesis are also unclear: 1) what effects the anodization treatment of carbon-based electrodes will make on their catalytic performance for the HER; 2) what is the relationship between anodization conditions and catalytic properties; 3) why the anodization process can influence the HER activity.

With the above questions, in the present work we evaluated the effects of electrochemical anodization of home-made SPCEs on their activity for the HER, and found that a simple anodization process applied on newly-prepared SPCEs could prominently improve their catalytic properties for hydrogen evolution in acidic media. Impacts of anodization conditions including electrolyte, polarization time, and applied potential on the activity enhancement of treated SPCEs were investigated. Similar results were also verified in GCEs and carbon nanotube-modified electrodes. By probing the surface chemistry changes of SPCEs before and after treatment, the underlying mechanisms for the HER activity enhancement were finally clarified.

## 2. Experimental

### 2.1. Chemicals and materials

$\text{H}_2\text{SO}_4$ ,  $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ , and  $\text{NaOH}$  were purchased from Sinopharm Chemical Reagent Co. Stock solutions of 0.5 M  $\text{H}_2\text{SO}_4$ , 1.0 M phosphate buffer solution (PBS, pH 7.0), and 1.0 M  $\text{NaOH}$  were prepared for use. Deionized water was utilized throughout the study. Multi-walled carbon nanotubes (MWCNTs, >95% in purity, 10–20 nm in diameter, and 10–30  $\mu\text{m}$  in length) were purchased from Beijing Daojin Technology & Science Co. Before use, the received MWCNTs were pre-treated according to the literature [34].

### 2.2. Anodization treatment of electrodes

Lab-made SPCEs were fabricated using a commercial graphite-based printing ink (Electrodag-423SS, Acheson Co.) according to the previous work [35]. GCEs (Shanghai Chenhua Instruments Co.) were polished with metallographic abrasive papers and slurries to create a mirror finish and then cleaned with adequate ethanol and water. MWCNT-modified GCEs were fabricated by casting 10  $\mu\text{L}$  of a 5  $\text{mg mL}^{-1}$  MWCNT suspension onto the working surface of cleaned GCEs for dry at room temperature. Anodization treatment was carried out on a CHI660E electrochemical workstation (Shanghai Chenhua Instruments Co.) with a three-electrode configuration composed of an SPCE (or GCE, or MWCNT-modified GCE) working electrode, a Pt wire counter electrode, and a saturated  $\text{Ag}/\text{AgCl}$  reference electrode (0.205 V vs. RHE). Simply, a constant potential was applied on the working electrode immersed in different electrolytes for a certain of time. After treatment, the working electrode was rinsed with adequate water and dried at room temperature for evaluation.

### 2.3. Electrochemical evaluation

All HER measurements were performed in 0.5 M  $\text{N}_2$ -saturated  $\text{H}_2\text{SO}_4$  at room temperature, with the above electrochemical configuration. Linear sweep voltammograms (LSVs) were recorded at a scan rate of 5  $\text{mV s}^{-1}$ . Tafel plots were derived from the LSVs at low potentials. Electrochemical impedance spectroscopy (EIS) was carried out at  $-0.9\text{ V}$  vs.  $\text{Ag}/\text{AgCl}$  with a frequency range from 100 kHz to 1 Hz and a 5 mV AC bias. The chronoamperometric measurement lasted for 4 h at a constant potential of  $-0.9\text{ V}$  vs.  $\text{Ag}/\text{AgCl}$ . All potentials reported for the HER were  $iR$  corrected and referred to the RHE by adding a value of 0.205 V.

### 2.4. Characterization

The surface morphology of SPCEs before and after anodization was observed on a field-emission scanning electron microscope (FESEM, S-4800, Hitachi High Technologies Co.). X-ray photoelectron spectra (XPS) were acquired on an ESCALAB-250Xi spectrometer (Thermo-Fisher, USA). The hydrophilicity experiment was carried out on a KSV CM200 optical contact angle meter (Finland Attention Co.). Raman measurements were finished on a DXR Raman spectrometer (Thermo-Fisher, USA) with a 532 nm laser source and a power of 8 mW.

## 3. Results and discussion

Compared to other processes such as mechanical polishing, laser exposure, and plasma treatment, electrochemical anodization, with no requirement for specific equipments and boring operations, seems to be a simpler method for electrode treatment. In the present work a common chronoamperometry technique was used for the anodization of newly-prepared SPCEs in three different electrolytes, i.e., 0.5 M  $\text{H}_2\text{SO}_4$ , 1.0 M PBS (pH 7.0), and 1.0 M  $\text{NaOH}$ . Fig. 1 compares the chronoamperometric curves of SPCEs in these electrolytes by applying a constant potential of 2.0 V vs.  $\text{Ag}/\text{AgCl}$ . Clearly, anodic currents are observed in all of the three electrolytes. This implies that some oxidation reactions occur on the SPCE surface. Interestingly, in the alkaline  $\text{NaOH}$  solution a much larger current is recorded compared to those in the acid and neutral electrolytes, revealing that the anodization degree of SPCEs in such an alkaline medium is higher under other identical conditions.

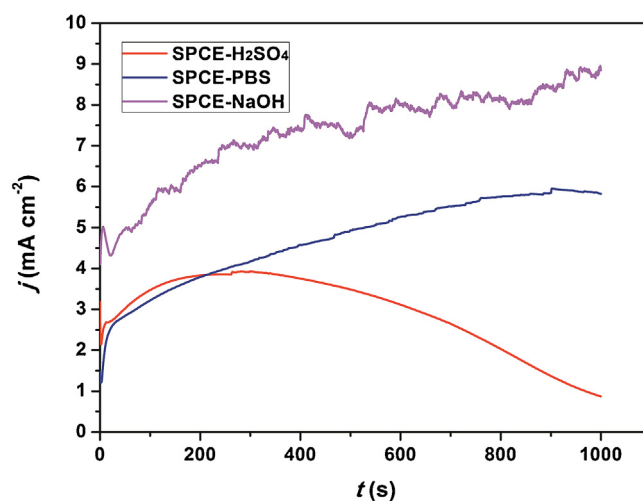


Fig. 1. Chronoamperometric curves of SPCEs anodized in different electrolytes at 2.0 V vs.  $\text{Ag}/\text{AgCl}$  for 1000 s.

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