

Salts of $C_{60}(OH)_8$ Electrodeposited onto a Glassy Carbon Electrode: Surprising Catalytic Performance in the Hydrogen Evolution Reaction**

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With the energy crisis becoming increasingly serious, hydrogen is proposed as a promising energy carrier substitute to fossil energy. A practical technique to produce hydrogen is the splitting of water by either electrochemical or photochemical methods.^[1] Usually, catalysts are widely used to overcome the overpotential for the hydrogen evolution reaction (HER) and to obtain high efficiency. Among the catalysts produced for the HER, Pt, Pd, and Ru show the best performance, but their high cost seriously limits their use. On the other hand, less expensive substitutes using metals such as Ni and Co suffer from corrosion, passivation, and lower catalytic activity.^[2] The need for active, stable, and inexpensive electrocatalysts has aroused intensive research interest, resulting in the development of molecular catalysts. Thus far, relatively few molecular catalysts have been studied for the HER in aqueous solutions, and most of catalysts studied consisted of transition metals.^[3] Herein, we report a novel molecular catalyst based on carbon: a salt consisting of fullerene anions electrodeposited onto a glassy carbon electrode (GCE) coated with Nafion in an aqueous solution for the HER. The onset potential was estimated to be -0.11 V (vs. RHE) with low loading and high exchange current density.

Polyhydroxylated fullerene (fullerenol) is one of the most studied fullerene derivatives, because of their low biological toxicity and outstanding radical scavenging ability.^[4] Various synthetic methods have been reported,^[5] but most of them obtained complicated mixtures of fullerenols with different structures, which limited further study of their properties. We have previously reported the preparation of the first isomerically pure multihydroxylated fullerene, $C_{60}(OH)_8$.^[6] Its sol-

ubility in water is much greater than that of C_{60} due to the eight hydroxy groups on the carbon cage, which makes it possible to study its electrochemical properties in aqueous solutions; these properties are fundamental for investigating electrocatalysis based on fullerenols. There have been few reports to date about the electrochemical properties of fullerenols in water,^[7,8] therefore, we investigated electrochemical behavior of $C_{60}(OH)_8$ in aqueous solutions.

Figure 1 displays a cyclic voltammogram of $C_{60}(OH)_8$ in an aqueous solution of KCl (0.1 M). A reduction peak at

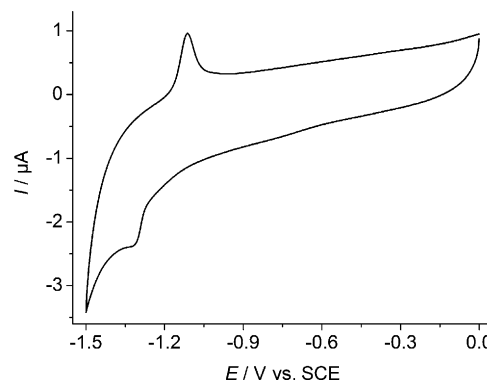


Figure 1. Cyclic voltammogram of $C_{60}(OH)_8$ ($5 \mu\text{M}$) on a GCE in an aqueous solution of KCl (0.1 M) at a scan rate of 0.1 V s^{-1} .

-1.31 V (vs. SCE) and an oxidation peak at -1.11 V were observed. The experimental results indicated that the cations of the supporting electrolyte influenced the electrochemical behavior of $C_{60}(OH)_8$. Optimal current responses were obtained in NaCl and KCl solutions, and their redox peak potentials were identical. The possible explanation is that the sizes of sodium and potassium cations are more suitable for intercalation into the lattice of $C_{60}(OH)_8$ crystals to compensate for the negative charge and stabilize its crystal structure upon electrochemical reduction of $C_{60}(OH)_8$. Therefore, NaCl and KCl were chosen as the supporting electrolytes for the following work. To illustrate the electrochemical reaction mechanism of $C_{60}(OH)_8$ in an aqueous solution, the electrochemical behavior of $C_{60}(OH)_8$ in *N,N*-dimethylformamide (DMF) was also investigated by cyclic voltammetry. Three reduction peaks on an initial scan to negative potentials and three oxidation peaks on the reverse scan were observed (Supporting Information, Figure S1). The redox potentials ($E_{1/2}$) are -0.98 , -1.50 , and -2.12 V (vs. Fc^+/Fc), respectively. Compared to the electrochemistry of pristine C_{60} under

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similar conditions,^[9] they corresponded to three-step reductions and reoxidations of $C_{60}(OH)_8$, and they are shifted to more negative potentials, owing to the addition of hydroxy groups on the C_{60} cage. Based on this, and the reported electrochemistry of C_{60} films in a mixture of DMF and water,^[10] we concluded that the redox peaks of $C_{60}(OH)_8$ in aqueous solution corresponded to a one-electron-transfer reduction and reoxidation.

The influence of scan rate was also studied (Figure S2). The reduction peak current had a linear relationship with the square root of the scan rate in the range of 0.02–0.5 $V s^{-1}$, which suggested that the reduction peak was a diffusion-controlled wave. From the peak shape of the reoxidation peak, we presumed that the reoxidation peak might be a stripping process. This was verified by experimental results showing that the reoxidation peak current increased as the deposition time increased at a deposition potential of –1.50 V (vs. SCE), and that the reduction peak current showed no significant change (Figure S3). Therefore, we concluded that one $C_{60}(OH)_8$ molecule obtained one electron to form a $C_{60}(OH)_8$ anion during the reduction process, the $C_{60}(OH)_8$ anion combined with cation of the supporting electrolyte to form a “ $C_{60}(OH)_8$ anion salt”, and then deposited onto the surface of the electrode. Upon reoxidation, the $C_{60}(OH)_8$ anion salt on the electrode was stripped into the solution.

Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) characterizations also attested to this. As shown in Figure 2 (see also Figure S4), some microparticles were deposited on the GCE after being electrolyzed at –1.50 V for 120 s, and they resulted from aggregates of the $C_{60}(OH)_8$ anion salt; $C_{60}(OH)_8$ also has a strong tendency to form aggregates.^[11] The deposited

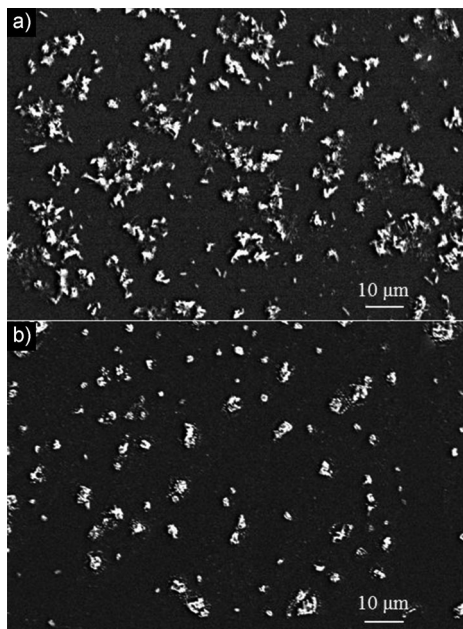


Figure 2. SEM images of a GCE modified with the $C_{60}(OH)_8$ anion salt before (a) and after reoxidation scanning at –1.5–0 V (b) using differential pulse voltammetry.

microparticles decreased visibly during the scan from –1.50 to 0 V, which supports the deposition–stripping process. The poor reversibility of the reduction of $C_{60}(OH)_8$ resulted in not all of the deposited particles being released into the solution. XPS analysis (Figure S5) indicated that the electrodeposited $C_{60}(OH)_8$ anion salt was composed of the elements C, O, and Na (hydrogen cannot be detected). Furthermore, the amount of sodium deposited on the electrode decreased visibly after reoxidation. These results also verified that sodium cations combined with $C_{60}(OH)_8$ anions to form the salt deposited on the electrode surface during the reduction process. Meanwhile, experimental results revealed that the large ionic strength was helpful for the electrodeposition of the salt and its stripping upon reduction and reoxidation (Figure S6A), which conformed to the electrodeposition condition requirement of high conductivity.

Taking into account the possible interaction between $C_{60}(OH)_8$ and H^+ , as well as the potential application of fullereneols as proton conductors,^[8,12] the electrocatalytic activity of the obtained $C_{60}(OH)_8$ anion salt on the GCE toward the HER was also investigated. To inhibit the dissolution of electrodeposited microparticles on the GCE into the solution, Nafion was dropped onto the surface of an electrode modified with the $C_{60}(OH)_8$ anion salt to form a Nafion/ $C_{60}(OH)_8$ salt modified GCE. Figure 3 shows the

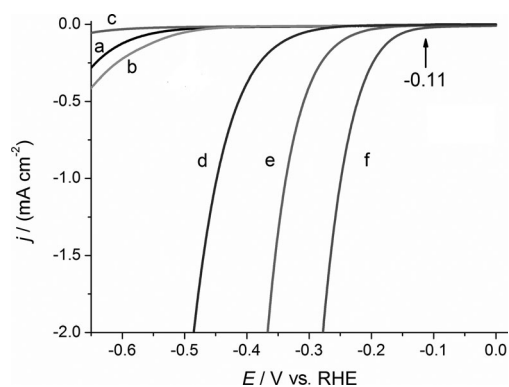


Figure 3. Polarization curves of a) bare GCE, b) bare GCE coated with Nafion, c) C_{60} modified GCE, d) $C_{60}(OH)_8$ modified GCE, e) $C_{60}(OH)_8$ anion salt modified GCE, and f) Nafion/ $C_{60}(OH)_8$ salt/GCE. All performed in H_2SO_4 (0.5 M) at a scan rate of 2 $mV s^{-1}$. See the Supporting Information for experimental details.

catalytic performance of different electrodes for the HER. The best result was obtained from the electrode modified by the deposited $C_{60}(OH)_8$ anion salt, which was prepared in an aqueous solution of $C_{60}(OH)_8$ (5 μM) containing KCl (0.5 M) at –1.50 V (vs. SCE) for 120 s and coated with Nafion films. Hydrogen evolution was observed at –0.11 V (vs. RHE), which is comparable to results with MoS_2 on the electrodes.^[13]

The Tafel plot fit well with the Tafel equation when the overpotential was between 0.11 V and 0.25 V, as shown in Figure 4, and the Tafel slope was calculated to be 78 $mV dec^{-1}$, which means that the HER occurs through a Volmer–Heyrovsky mechanism.^[14] The rate determining step is the electrochemical desorption of an adsorbed hydro-

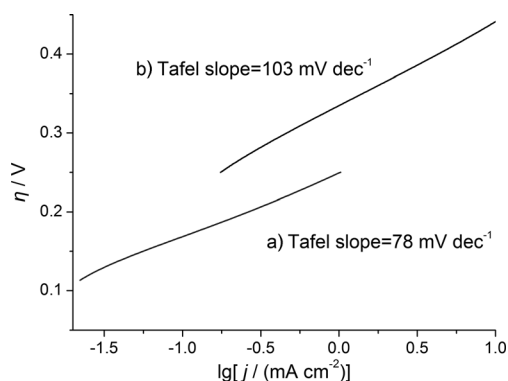


Figure 4. Tafel plots of a) the Nafion/ $C_{60}(OH)_8$ salt/GCE and b) GCE modified with the $C_{60}(OH)_8$ anion salt. Performed in H_2SO_4 (0.5 M) at a scan rate of 2 mV s^{-1} , and corresponding to Figure 3 e and f.

gen atom and H_3O^+ to form hydrogen, based on the corresponding Tafel slopes of three predominant reactions for the HER on a metal catalyst. Compared with a Tafel slope of 103 mV dec^{-1} and an onset potential of -0.16 V for the HER at the electrode modified with $C_{60}(OH)_8$ anion salt, but without Nafion (Figures 3 and 4), it was concluded that the presence of Nafion not only acted as a proton-exchange membrane to permit effective transportation of hydrogen ions, but also suppressed the stripping of the electrodeposited $C_{60}(OH)_8$ anion salt, thus much more electrocatalyst was retained on the GCE. To test this, the electrode modified with the electrodeposited $C_{60}(OH)_8$ anion salt was taken out of the solution containing $C_{60}(OH)_8$, washed with water, and then put into a solution containing KCl (0.5 M) and a continuous electrochemical scan from -1.5 V to -0.8 V was performed by differential pulse voltammetry (DPV). It was found that the reoxidation peak current gradually decreased, and the reoxidation peak nearly disappeared after three scans (Figure S7). The electrode was used to test the HER, but no electrocatalytic activity was observed. However, when Nafion was coated onto the surface of the electrode modified with the electrodeposited $C_{60}(OH)_8$ anion salt and the same tests were done, no reoxidation peak was observed by DPV and good electrocatalytic activity for the HER was obtained. These also provided support for the stripping of the $C_{60}(OH)_8$ anion salt upon reoxidation at the modified electrode without Nafion. The exchange current density was calculated to be $7.0 \times 10^{-7}\text{ A cm}^{-2}$, which was on the same order of magnitude as the well-developed molybdenum and tungsten sulfide catalysts.^[13] The approximate loading of the salt was $2\text{ }\mu\text{g cm}^{-2}$, which was much smaller than the different reported MoS_x and WS_2 catalysts (see the Supporting Information for these calculations).^[13] All of these results indicated the excellent electrocatalytic performance of the $C_{60}(OH)_8$ anion salt with Nafion films for the HER.

The experimental results suggested that the ionic strength for the electrodeposition of the $C_{60}(OH)_8$ anion salt similarly influenced the electrocatalytic activity of the HER. The large ionic strength was helpful for enhancing the catalytic activity in $0.05\text{--}0.5\text{ M}$ KCl (Figure S6). One possible reason for this is the increase of the deposited loading of the $C_{60}(OH)_8$ anion

salt on the electrode. However, when the electrodeposition was performed in concentrations of KCl larger than 0.5 M , the catalytic performance was poor, which may result from the larger loading on the electrode leading to poor conductivity, as in our previous work.^[15]

A possible explanation for high electrocatalytic activity of the $C_{60}(OH)_8$ anion salt toward the HER can be deduced from the following two aspects: 1) The adsorption of H^+ onto the $C_{60}(OH)_8$ anion salt is relatively easy. As fullerenols have been reported to act as proton conductors,^[8,12] it is facile to form hydrogen bonds between H^+ and oxygen atoms in the $C_{60}(OH)_8$ anion. Furthermore, the $C_{60}(OH)_8$ anion salt, which is negatively charged, is helpful for the adsorption of H^+ , owing to electrostatic interactions. The adsorption of H^+ on these oxygen atoms leads to hydrogen evolution. This is similar to the origin of MoS_2 and WS_2 for the HER, which is ascribed to the adsorption of H atoms on the unsaturated sulfur atoms at the edge.^[16] The fact that the C_{60} modified electrode exhibited an inferior catalytic activity for the HER also provides support for this, as shown in Figure 3. In addition, the location of all the OH groups of the fullereneol $C_{60}(OH)_8$ molecule in the same hemisphere may produce a good structure for hydrogen evolution. 2) The $C_{60}(OH)_8$ anion salt deposited on the GCE showed good conductivity, which was verified by electrochemical impedance measurements (Figures S8 and S9). The charge transfer resistance of the Nafion/ $C_{60}(OH)_8$ salt/GCE decreased as the overpotential increased at $100\text{--}240\text{ mV}$, and they were much lower than those of the bare GCE and the $C_{60}(OH)_8$ modified GCE. Effective electrical coupling of the electrodeposited $C_{60}(OH)_8$ anion salt to the GCE resulted in much faster HER kinetics, as with MoS_2 nanoparticles grown on graphene.^[17]

The durability of the electrode modified with the electrodeposited $C_{60}(OH)_8$ anion salt for the HER was also tested. After 1000 scanning cycles, a polarization curve for the HER similar to that before testing was observed, with a negligible decrease in the cathodic current (Figure 5). The good stability of the Nafion/ $C_{60}(OH)_8$ salt/GCE was attributed to the Nafion film, as it inhibited the stripping of the $C_{60}(OH)_8$ anion salt.

In summary, we have prepared an electrode modified with an electrodeposited $C_{60}(OH)_8$ anion salt and coated with

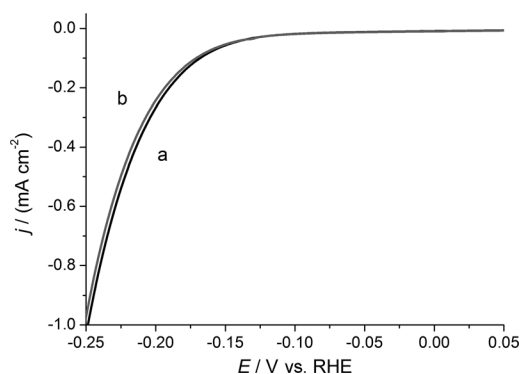


Figure 5. Stability test for the Nafion/ $C_{60}(OH)_8$ salt/GCE. Polarization curves of the first scan (a) and after 1000 cycles of cyclic voltammetric scanning (b) in H_2SO_4 (0.5 M) solution at a scan rate of 2 mV s^{-1} .

Nafion. This system was developed by investigating the electrochemical behavior of $C_{60}(OH)_8$ in water on a GCE. It showed good catalytic performance in the HER with an onset potential of -0.11 V and an exchange current density of $7.0 \times 10^{-7} \text{ A cm}^{-2}$ at a loading of about $2 \mu\text{g cm}^{-2}$. This study provides a new kind of molecular catalyst, based on fullerene derivatives without transition metals, for the HER. We anticipate our discovery to be the starting point for exploring more effective all-carbon-based non-metal molecular catalysts for the HER. Further work will involve the study of other fullerene derivatives with polar groups, such as sulfo groups, carboxyl groups, and different numbers of hydroxy groups on the fullerene cage, as molecular catalysts for the HER.

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