Enhancement of Hydrogen Insertion into Carbon Interlayers by Surface Catalytic Poisoning

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The well-known phenomenon that the adsorption of catalytic poisons can promote H electrosorption into metal electrodes is demonstrated on carbon electrodes for the first time. The use of a small amount of thiourea in the KOH electrolyte as a catalytic poison can substantially enhance the H insertion into the carbon interlayer. The mechanism of such a promotion of H insertion by the catalytic poison is proposed. The adsorbed thiourea interferes with the H + H recombination, thus the competitive hydrogen evolution step is discriminated against in favor of H insertion into the carbon interlayer. The increase of current efficiency for H insertion is the supporting evidence for such a mechanism. ac impedance and equivalent circuits are also used to investigate the surface phenomena and proton diffusion. Evidently, although the thiourea stays on the surface during reduction, the electrosorbed thiourea may become oxidized and desorbed from the surface at the oxidation overpotential. It is demonstrated that the strong surface adsorption of the poison species could significantly reduce self-discharge or leakage of hydrogen at the open-circuit voltage and favorably impact the kinetics for hydrogen oxidation.

I. Introduction

Hydrogen, which can be produced from renewable energy sources and burn pollution-free, could eventually replace fossil fuels and dramatically reduce the emission of greenhouse gases. Safe and reversible storage of hydrogen are two of the crucial technical challenges for the application of hydrogen as a competitive energy carrier. Unfortunately, there is not yet a storage method that can meet the requirements for safety and effectiveness. Besides hydrogen compression and liquefaction under cryogenic conditions, chemical hydrides, and gas-on-solid adsorption, the direct adsorption of hydrogen generated by water electrolysis into a host electrode material offers unique advantages for storing hydrogen under ambient conditions.[1] The phenomenon of hydrogen adsorption onto Pd was first reported by Graham.[2] Similar behavior has been reported on various transition metal electrodes such as Fe, Ti, Zr and especially mischmetal alloys, which have been used as anode materials for rechargeable Ni–MH batteries and played a role in replacing the once widely used toxic Ni–Cd batteries. Recently, hydrogen was also found to be adsorbed into carbon interlayers electrochemically,[3] and the potential for using carbon material as the vehicle for hydrogen storage has been discussed.[4–6] Electrochemical H sorption originates from the deposition of H atoms at the carbon surface. The adsorbed H at the surface can then diffuse to the edge orientation where it diffuses into the carbon interlayer space in competition with parallel electrochemical or chemical recombination processes, in which H_2 is formed and subsequently departs the electrode's surface. It is also well-known that cathodic H sorption into metals or alloys can be greatly enhanced by the presence of so-called catalytic poisons, for example, H_2S, thiourea, As_2O_3, and so forth.[7–11] Although the mechanism of the catalytic poison is still under debate, several possible mechanisms were proposed by Conway and co-workers. It is often proposed that the poison blocks H + H

recombination, facilitating the entry of the adsorbed H into the metal. However, this mechanism is difficult to reconcile with the diminished H coverage caused by adsorption of poison ions and the irrelevance of the H + H recombination process for most of the transition metal electrodes.[11] The chemical potential of H for a particular H coverage could be enhanced by the competitive adsorption of poison ions due to the increase of the configurational activity quotient,[7] which could weaken the chemisorption bond of H and thus enhance the driving force for the insertion of H into carbon interlayer. Qian and Conway reported that the presence of AsO_2^- significantly enhanced H permeation into Fe or mild steel.[10] The mechanism for the enhancement was proposed: the adsorbed AsO_2^- became reduced to AsH_3 gas at a high overpotential, causing desorption from the electrode's surface. The newly vacant active sites were available for H adsorption at a high overpotential, increasing the H coverage.[10] It is the first time, however, such enhancement of hydrogen adsorption on a carbon electrode due to a catalytic poison is reported and a possible mechanism is postulated.

II. Experimental Methods

High surface area carbon material (M-20) was obtained from Spectrocorp USA, Norit-E and Norit-A were obtained from Norit, and PWA was purchased from Calgon Carbon. The comparison of pore size distribution for the carbon materials is shown in Figure 1. The particle size of the carbon materials is in the range of 10–20 μm. The detailed analyses of all the carbon, for example, surface area, d_{002}, and so forth, were reported previously.[3] Thiourea and L-cystine were purchased from Sigma-Aldrich. To make an electrode, the carbon material was first mixed with 10 wt % (dry material) of a Teflon suspension (DuPont T-30) as a binder. The resulting Teflonized carbon was left to air-dry before being hot-rolled to form a flexible thin film. The electrode was then punched out of the big sheet. The thickness of the electrode was 0.2 mm. Two pieces of these carbon electrodes were sandwiched between a Ni current collector and housed in a Teflon screw-plug holder.

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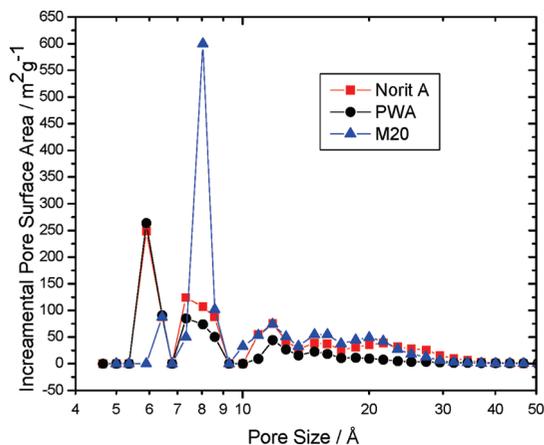
Figure 1. Comparison of pore size distribution of Norit A, PWA, and M20 activated carbon materials.

The electrode holder resided in the center of a large Pt mesh net counter electrode. A Hg/HgO reference electrode was put close to the electrode holder. The electrodes were anodically and cathodically polarized in either 30 wt % KOH or 30 wt % KOH with 0.0003 M poison compounds, for example, thiourea or L-cystine. The detailed description of the cell holder and the procedures for the subtraction of double-layer capacitance can be found in the previous publication.[3]

An EG&G 170 potentiostat/galvanostat controlled by the Q&R Smart Data package was used for electrochemical measurements. A Micromeritics ASAP 2020 porosimeter was used for the surface area and porosity measurements. Nitrogen was used as absorbent gas. Density functional theory (DFT) software from Micromeritcs was also used.

III. Results and Discussion

The mechanism of H sorption into pristine carbon electrodes was reported by us previously.[3] Similar to the mechanism of H sorption into metal electrodes, for example, Pd,[12] electrochemically adsorbed H originates from H atoms discharged from H_2O molecules at the carbon surface. The driving force for the insertion process is a chemical potential gradient associated with the H coverage on the carbon surface and H concentration in the interlayer space; both are a function of electrode overpotential and H host interactions. After being adsorbed on the electrode's surface, the H can then migrate to the edge orientation of the microdomains of defective graphene layers, where it diffuses into the carbon interlayer space in competition with the parallel electrochemical or chemical recombination processes, in which H_2 is formed and subsequently departs the electrode's surface.[3] It has been demonstrated that when the H coverage (θ_H) on the carbon surface approaches 1, or the increase of overpotential is beyond the value required for θ_H to be attained, the discharged H is combined to form H_2. The current-efficiency for H sorption was then diminished. The amount of hydrogen adsorbed was found to be related to the carbon interlayer distance (d_{002}), where the carbon with a larger interlayer distance would accommodate more H atoms.[3]

Because of the mechanistic similarity of electrochemical adsorption of hydrogen into both metal lattices and carbon interlayers, it is reasonable to predict that the well-known promotion of H sorption by catalytic poisons, such as H_2S, thiourea, and As compounds, may be effective on the carbon electrode as well. Even though the origins of the catalytic poison effect still remain unclear, for the first time, the facilitation of H sorption by the adsorption of the catalyst poison on the carbon
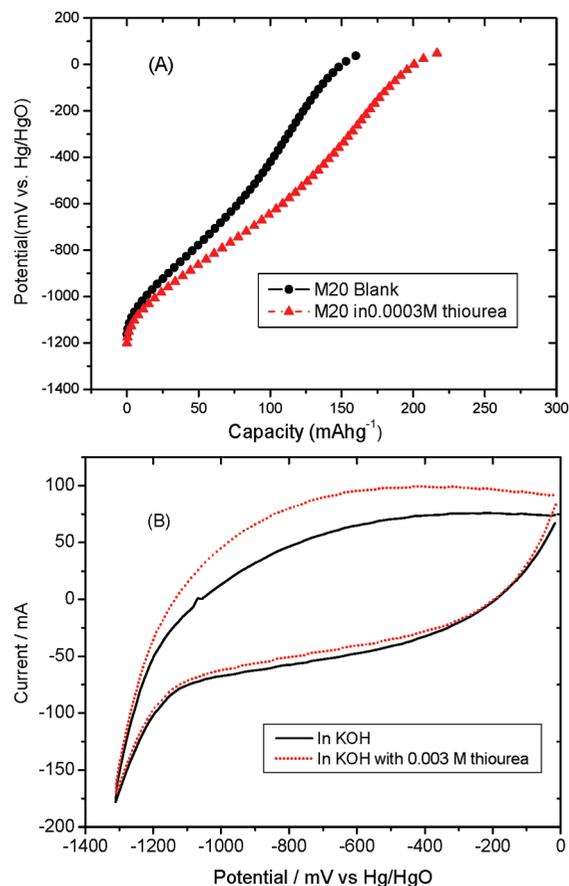
Figure 2. Comparison of the oxidation of atomic hydrogen electrochemically stored in M-20 activated carbon electrode in 30% KOH with or without 0.0003 M thiourea. Both electrodes were polarized under the same constant anodic current density (56 mAg^{-1}) (A); comparison of cylicvoltammetry profiles of the same electrodes, scan rate: 1 mVS^{-1}.

electrode is demonstrated as shown in part A of Figure 2, which shows a comparison of electrochemical oxidation of the atomic hydrogen stored in an M20 activated carbon electrode in the alkaline electrolyte with and without the presence of thiourea as the catalytic poison. Thirty percent more hydrogen is demonstrated to be inserted into the carbon interlayers, reversibly, for the electrode with exposure to thiourea than the one without exposure to thiourea. Both electrodes were first fully charged under the same conditions before discharge. M-20 is among those with the largest d_{002} value. Part B of Figure 2 shows a comparison of the cyclicvoltammetry of the same electrodes. The phenomenon of such enhancement of H insertion by catalytic poisons are found in various carbon materials and different poison catalysts. Figure 3 shows the comparison of the electrodes made with Norit A activated carbon material discharged in pure 30 wt % KOH and the electrolytes with additives of 0.0003 M L-cystine and 0.0003 M thiourea, respectively. It seems that different poison catalysts enhance the H insertion differently, although both of the catalysts increase the amount of H sorption in the carbon electrode. Table 1 tabulates the results of the electrodes made with various high-surface area carbon materials. Table 1 shows that the enhancement of H sorption can be found in all carbon electrodes.

The proposed mechanism is shown in Figure 4. In the process of electrochemical water decomposition, H_2O molecules gain electrons from the carbon anode and hydrogen atoms are formed at the surface of the anode. The H remains electrosorbed on the surface of the carbon electrode (Volmer reaction): C(e) +
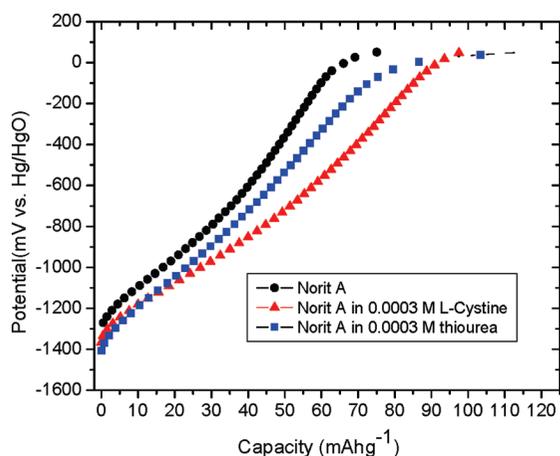
Figure 3. Comparison of the oxidation of atomic hydrogen electrochemically stored in Norit A activated carbon electrolyte in 30% KOH, the electrolyte with L-cystine or thiourea additives.

$H_2O \leftrightharpoons CH_{ads} + OH^-$. There could be two competitive paths for the adsorbed H.

• Hydrogen recombination through either desorptive recombination (Tafel reaction): $2CH_{ads} \leftrightharpoons H_2 + C$ or atom-ion electrodesorption of H (Heyrovsky reaction): $CH_{ads} + C(e) + H_2O \leftrightharpoons H_2 + OH^-$.

• H intercalation/insertion into the lattice of the host material, for example a metal alloy or interlayer of carbon.

The H atoms residing on the surface can either diffuse close to each other on the surface of the carbon electrode to recombine and form H_2 or can intercalate into the interlayer of carbon from the edge orientations. The H intercalation reaction would be the dominant reaction at low surface coverage of electrosorbed H, because the rate of H_2 evolution is proportional to the degree of H monolayer coverage on the electrode's surface. The intercalation process proceeds until the majority of the surface is covered with a monolayer of electrosorbed H, allowing a significant amount of H_2 to be generated.[3] The hypothesis is that the poison impedes H + H recombination and thus the entry of the adsorbed H into the carbon interlayer is promoted by inhibiting the parallel competitive process of forming H_2. With the help of a surface poison, H could intercalate into the carbon interlayer even if there is a high H coverage on the electrode. Thiourea is known to be a strong adsorbent with the donor S atom, which could bond to the unsaturated edge plane or the defect sites on the carbon microdomains. The sorption of catalytic poisons generally blocks electrode surface sites, diminishing the coverage by adsorbed H, which is the intermediate resulting from the discharge of H^+ ions in the cathodic H_2 evolution reaction. Those poison species could serve as geometrical spacers, which prevent the two adsorbed hydrogen atoms from getting close enough to each other to form H_2. Thus, even though the catalytic poisons reduce the fractional coverage of adsorbed H, they can actually enhance H insertion into the electrode.

The hypothesis for the mechanism seems to be consistent with the evidence illustrated in Figure 5. Hydrogen is inserted into the carbon interlayer space by first anodically charging the electrode to various capacities, and then the hydrogen in the carbon interlayers releases during the cathodic discharge. The relationship between the efficiency, which was defined as the ratio of discharge/charge capacity, and charging capacity is shown in the figure. It has been demonstrated that when the H coverage (θ_H) on the carbon surface approaches 1, or the increase of overpotential is beyond the value required for to

attain θ_H, the discharged H atoms combined to form H_2. The current efficiency for H sorption was diminished.[3] Even though the electrodes with and without the presence of thiourea demonstrate close to 100% efficiency at low charging capacity, which is equivalent to the low surface H coverage, the efficiency for the electrode without thiourea decreases rapidly as the H coverage increases. The efficiency for the electrode with the poison catalyst is at around 50% at high charge capacity while the electrode without the poison catalyst dropped close to 30%. It seems that, before electrosorbed H reaches high coverage, the majority of the H atoms on the edge surface become inserted into the carbon interlayer, and can be subsequently released during the cathodic discharge. When the high surface coverage of H is reached, substantially less H atoms recombine with their neighbors and become H_2 on the electrode modified with poison catalyst due to the catalytic poison blocking effect. Instead, the single H atoms continuously intercalate into the carbon interlayer.

Although the experimental evidence supports the hypothesized mechanism that poisons block H + H recombination and thus favor the entry of adsorbed H into the carbon interlayers, as mentioned previously, the mechanism is difficult to reconcile with the following: the competitive adsorption of poison species diminished the fractional coverage of H and the irrelevance of recombination control at most transition metal electrodes.[11] Becaise the C=S bond is found to be reactive in both the reduction and oxidation of thiourea,[13] the adsorbed poison can become desorbed during strong cathodic or anodic polarization with the extent of desorption being dependent on the polarization potential and the electrochemical reactivity of the poison species on the surface.[9] During the initial treatment, the active sites occupied by the inherited carbon functional groups could be replaced by the S-containing poison catalysts, for example, thiourea, and such poison catalysts become progressively desorbed with increasing overpotential, creating a great deal of new active sites available for H adsorption. The thiourea was believed to be completely desorbed from the active sites on the metal electrode. To further investigate the catalytic poison mechanism for carbon electrodes, ac impedance measurements were conducted during the electrochemical H upload and discharge.

Figure 6 shows a comparison of typical impedance spectra for M30 activated carbon electrodes in KOH and in KOH with 0.0003 M thiourea. The equivalent circuit models for the numerical fittings are also shown in the figure. Two distinguishing features can be seen on both impedance spectra in Figure 6, which represent the two electrochemical processes. The semicircle in the high-frequency region results from the hydrogen redox reaction taking place on the surface of the carbon electrode and possibly from the poor electrode–current collector contact, which may not be applied in this case, because the low ohmic resistance demonstrates a good contact; the relatively straight line in the low frequency region represents the H diffusion into the carbon matrix. Thus, two different equivalent circuits were used to fit each electrochemical process. It seems both equivalent circuit simulate the spectrum of their corresponding frequency range very well.

It is assumed that hydrogen in H_2O gains an electron and becomes electrochemically absorbed onto the surface of the carbon electrode during the reduction process (charging), and the absorbed H losses an electron becoming an electrochemically absorbed H^+ during oxidation (discharge process). The charge transfer surface reactions are characterized by the Faradic resistance, R_{ct}, which can be represented as:
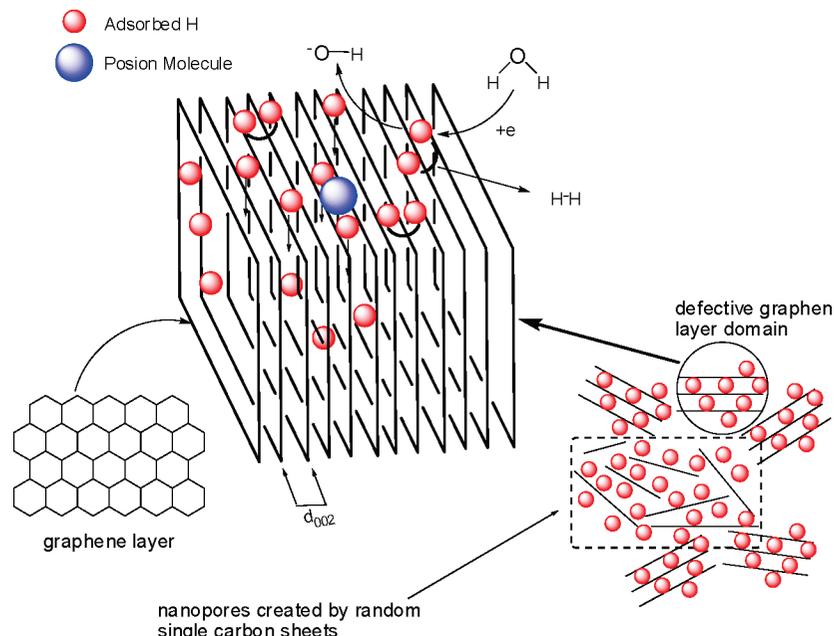
Figure 4. Illustration of H insertion into the carbon interlayer enhanced by surface adsorbed poison catalyst. Electrochemical H sorption originates from the formation of H atoms at the carbon surface. The adsorbed H diffuses into the carbon interlayer space in competition with the parallel electrochemical or chemical recombination process, in which H_2 is formed and subsequently departs the electrode surface. The recombination of two neighboring hydrogen atoms is impeded by the electrosorbed poison catalyst, which serves as a spacer between two hydrogen atoms.

TABLE 1: Comparison of the Electrochemical Hydrogen Storage for Various Carbon Electrodes in 30% KOH with and without Thiourea

carbon	discharge blank (mAh/g)	discharge poison (mAh/g)	improvement (%)	discharge after 48 h rest blank (mAh)	discharge after 48 h rest poison (mAh)	improvement (%)
M20	166	218	17	148	168	36
M30	145	171	31	71	93	32
Norit - E	71	78	9	33	47	17
PWA	59	69	17	28	42	47

$$R_{ct} = \frac{RT}{mFi_0}$$

Where i_o is the exchange current. The electrochemical double layer is established at the electrode−electrolyte interface. A constant phase element (CPE) is used in the equivalent circuit in place of a capacitor in parallel with R_{ct} to compensate for the nonhomogeneity of the high surface area porous carbon

electrode. Because the surface of a carbon material is normally covered with the surface functional groups and, for the carbon
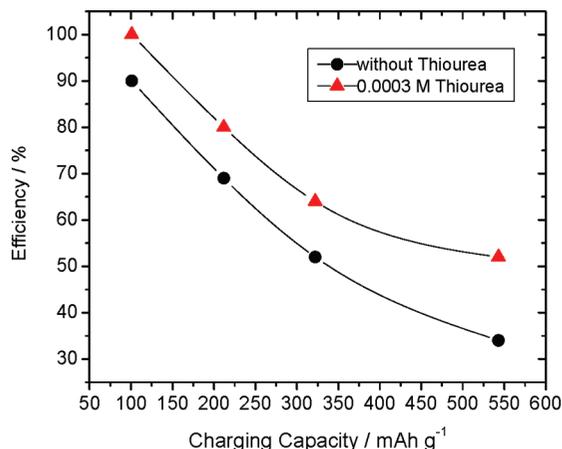
Figure 5. Discharge and charge efficiency for the hydrogen insertion with and without thiourea. The electrode was first chargeed at 100 mA g^{-1} for various durations and then discharged at 56 mA g^{-1}. The efficiency is defined as the percentage of oxidation capacity against reduction capacity.
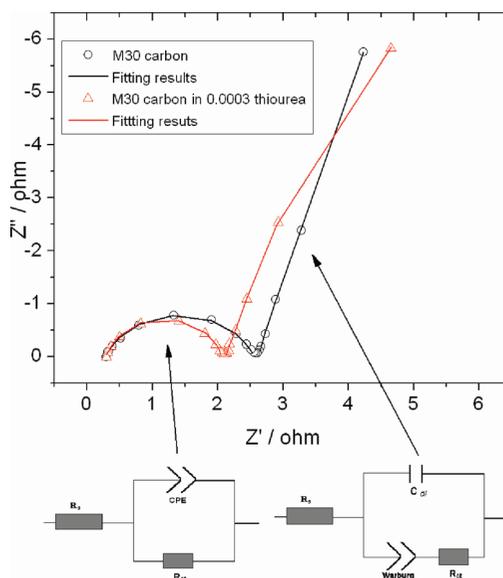
Figure 6. Comparison of typical ac impedance spectra for M30 activated carbon electrodes in 30% KOH with and without thiourea. The equivalent circuits (EC) used for the fitting of the ac impedance are listed. The EC on the left was used to fit the spectrum in the frequency range of 100 K to 1 Hz, and the EC on the right was used for the frequency range of 1 to 0.001 Hz. The fitting results are plotted as solid lines.
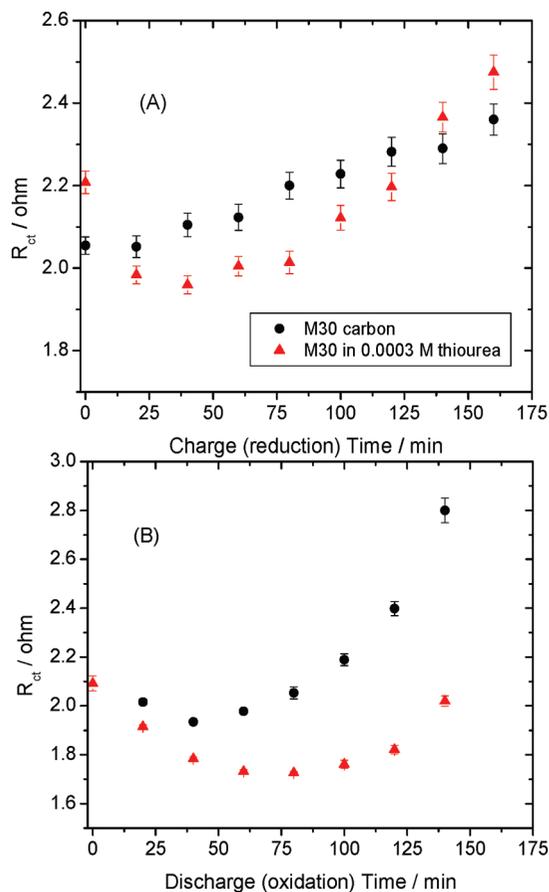
Figure 7. Comparison of the charge-transfer resistance, R_{ct}, for the electrodes in 30% KOH electrolyte with and without thiourea during reduction (A) and oxidation (B). R_{ct} was obtained by fitting the impedance spectra within 100 K to 1 Hz.

electrode in the KOH electrolyte containing thiourea, the surface is covered with thiourea, the capacitor represented by CPE would be the combination of double-layer capacitance and pseudocapacitance of surface groups on the carbon electrodes. Parts A and B of Figure 7 show the comparison of the change of R_{ct} for the electrodes made with M30 activated carbon material in the alkaline electrolyte with and without thiourea during reduction (charging) and oxidation (discharging), respectively. During the oxidation, R_{ct} stands for the Faradic resistance for hydrogen in a water molecule to gain one electron to become electrosorbed on the surface of the carbon material, whereas the R_{ct} in the reduction process represents the charge transfer reaction for electrosorbed H to lose one electron to become H_2O. As shown in part A of Figure 7, although the R_{ct} difference between the two electrodes was not very large throughout the reduction process, small but significant differences are observed in the first half of reduction. R_{ct} for the poisoned electrode is smaller than that of the nonpoisoned electrode. At the late stage of reduction, the R_{ct}'s for both of the electrodes merged. The activated carbon materials are normally covered with various kinds of surface functional groups, which behave differently during electrochemical polarization.[14] Because thiourea can be chemically absorbed on the surface of carbon strongly, it may replace the existing surface functional groups on the carbon surface. It is also noteworthy to emphasize that electrosorbed catalytic poisons may not only compete with H for the available adsorption sites but also interact with the H atoms on the surface. The hydrogen deposition can proceed at underpotential and/or overpotential conditions. The underpotential deposition is the deposition of

atoms or radicals over a range of potentials different from the thermodynamic potential for the formation of the corresponding bulk substance. It results from the fact that the interaction between the electrodeposited atoms and the substrate surface is stronger than that between the atoms of the substance in its bulk state. The competitive adsorption of the catalytic poison would have an impact on the kinetic behaviors of the hydrogen evolution reaction as well as the underpotential deposition of H. Lateral interactions among the adsorbed poison species and H could result in a change of H coverage at a given overpotential and modification of the surface electronic structure for the electrocatalysis.[10] Such an interaction may result in the small R_{ct} difference between poisoned and nonpoisoned electrodes in the early stage of discharge. Although additional research is needed to completely reveal the mechanism of such enhancement of electrochemical hydrogen adsorption and the nature of interatomic interactions, it appears that the poison catalyst only slightly affects on the charge-transfer resistance for the reduction process.

Part B of Figure 7 shows the changes of R_{ct} for both of the electrodes during the oxidation process. It is clear that the R_{ct}'s for both electrodes start at almost the same value. However, the R_{ct} for the carbon electrode in the solution with thiourea decreases in the beginning and only recovers in the later stage of oxidation. The R_{ct} for the electrode in the KOH electrolyte without the poison catalyst substantially increases after a very brief decline. It seems the surface poison catalyst could enhance the kinetics of the H oxidation reaction.

It was reported that the C=S bond can be reduced and oxidized.[13] However, recent studies[14,15] demonstrated that thiourea can be oxidized easily but is rather resistive to reduction. Thus, the adsorbed thiourea could be desorbed during the oxidation process. The departure of the adsorbed poison molecule could create new active sites for adsorption; a large portion of those sites were initially occupied by the native surface groups that were replaced by thiourea. This hypothesis is consistent with the results shown in parts A and B of Figure 7, in which the thiourea is shown to have little impact on the hydrogen reduction process, but significantly enhances the kinetics for the hydrogen oxidation process against the control. Figure 8 provides additional support for the hypothesis. The CPE-T, which in this case can be considered proportional to the double-layer capacitance and pseudo-capacitance of the porous carbon electrodes, is reasonably consistent during the reduction process for the electrode in the electrolyte with thiourea, as shown in part A of Figure 7. However, the CPE-T for the electrode with no poison catalyst changes significantly. Owing to the strong chemical interaction between the carbon surface and the C=S bond, a thiourea molecule would replace the other surface functional groups and remain on the surface during the reduction process. Consequently, the surface condition of the porous carbon electrode in the electrolyte with thiourea would remain unchanged during the reduction process. The capacitance of the electrode remains relatively stable. On the other hand, because a variety of functional groups attach to the carbon surface, the carbon electrode in the electrolyte without thiourea would display pseudocapacitance behavior due to the redox reaction of such functional groups. The pseudocapacitance contributes to the total capacitance represented by CPE-T, and the value of such capacitance varies with the electrode potential because different functional groups may react at different potentials.[16] Part B of Figure 8 shows the changes of CPE-T during the oxidation process. CPE-T for the carbon electrode in the electrolyte without thiourea changes with the

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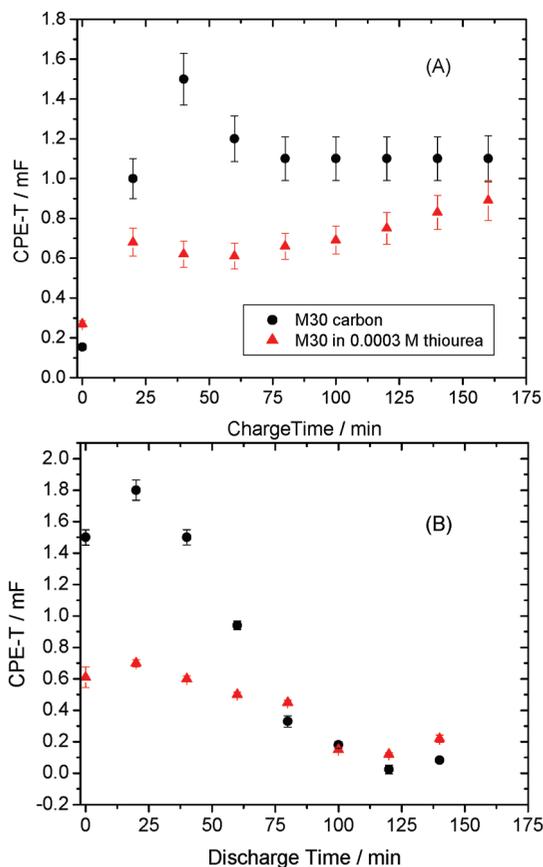
Figure 8. Comparison of the CPE-T, which is proportional to total capacitance of the electrode, for the electrodes in 30% KOH electrolyte with and without thiourea during reduction (A) and oxidation (B). CPE-T was obtained by fitting the impedance spectra within 100 K to 1 Hz.

Figure 9. Comparison of the oxidation of hydrogen electrochemically stored in PWA activated carbon electrode in 30% KOH with and without thiourea after resting at open circuit potential for 48 h. Hydrogen was preloaded into the electrode by the reduction in the electrolyte at 20 mA for 8 h.

oxidation time, because of the different pseudocapacitances at different electrode potentials as described previously. The CPE-T for the electrode in the electrolyte with thiourea, however, keeps decreasing as the oxidation proceeds. It is possible the phenomenon is due to thiourea being desorbed from the surface after being oxidized, and the capacitance decrease results from the loss of pseudocapacitance.

The assumption that surface poison catalysts remain on the carbon surface during the reduction process may be evident in Figure 9, which shows the comparison of self-discharge on the carbon electrodes in the electrolyte with and without thiourea. It is obvious that, after the 48 h storage at the open circuit potential, the same kind of carbon electrode in the electrolyte with thiourea retains substantially higher H in the interlayer. As shown in Figure 4, the H self-discharge takes place when hydrogen atoms in the interlayer diffuse to the surface carbon and become adsorbed to the surface. Two of the neighboring H atoms may recombine into H_2 and subsequently escape from the electrode surface. The H + H recombination process can be hindered with the surface catalytic poison, slowing the self-discharge process and retaining more hydrogen atoms in the carbon interlayer. If the thiourea on the electrode's surface becomes desorbed during oxidation, creating more active sites, then the H + H combination process will accelerate and less H will remain in the electrode. It is clearly inconsistent with the experimental evidence shown in Figure 9.

The proton diffusion within the carbon interlayer is also investigated through fitting the equivalent circuit. The low frequency region was used for the modeling, because the H
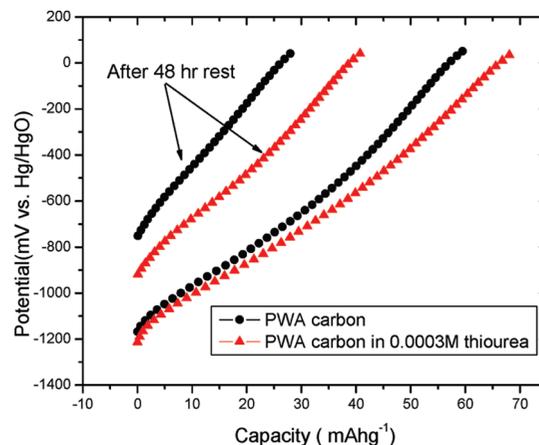
diffusion process is the rate-determining step. As shown in Figure 6, the Warburg impedance represents the proton diffusion through the carbon interlayer. The frequency of the modulation signal, alternatively the discharge current density, determines the depth the proton can travel. A lower frequency corresponds to a deeper diffusion into the material; a higher frequency corresponds to a shallower diffusion into the material. If the diffusion path is short enough, the proton will penetrate the entire thickness during the low frequency modulation, thus a finite Warburg impedance has to be used. On the other hand, if the available diffusion path is long enough, the proton cannot travel the entire length of the path even at the low modulation frequency or the low discharge current density ($\omega \gg D/\delta^2$, where ω is the modulation frequency, D is the diffusion coefficient of the charge carriers, and δ is the diffusion length). Then the impedance should be a semi-infinite Warburg impedance. The diffusion path for a proton into the carbon interlayer is the size of the graphite microdomain (L_c); because the high surface area carbon is very amorphous, the size of the microdomain is very small. Indeed, a finite Warburg component fit the ac impedance spectra much better than a semi-infinite model. Thus, a finite Warburg impedance was used to calculate the proton diffusion coefficient. A finite Warburg impedance can be expressed as:[15]

$$Z = (1 - i)\sigma\omega^{-1/2} \tanh \left\{ \delta \left(\frac{i}{\omega D} \right)^{1/2} \right\} \quad (1)$$

where δ represents the effective diffusion thickness and D is the effective diffusion coefficient of the particle.

$$Z_\omega = (1 - i)\sigma\omega^{-1/2} \tanh \left[\delta(i\omega/D)^{1/2} \right] \quad (2)$$

When

$$K = \sqrt{\frac{2\delta^2}{D}} \text{ or } D = \frac{2\delta^2}{K^{-2}} \quad (3)$$

Then

$$Z'_\omega(\text{real}) = \frac{\sigma}{\sqrt{\omega}} \frac{(\sinh K\sqrt{\omega} + \sin K\sqrt{\omega})}{(\cosh K\sqrt{\omega} + \cos K\sqrt{\omega}} \quad (4)$$

$$Z''_\omega(\text{imaginary}) = \frac{\sigma}{\sqrt{\omega}} \frac{(\sinh K\sqrt{\omega} - \sin K\sqrt{\omega})}{(\cosh K\sqrt{\omega} + \cos K\sqrt{\omega})} \quad (5)$$

Both σ and K can be obtained by means of the least-squares fitting of the ac impedance results. Parts A and B of Figure 9 show the comparison of K^{-2} changes on the carbon electrode in the electrolyte with and without thiourea during reduction and oxidation processes, respectively. As demonstrated in eq 3, the change of K^{-2} has the same trend as that of the diffusion coefficient (D). It seems the change of diffusion coefficients for the carbon electrodes in the electrolyte with and without catalyst poison follow the same trend during reduction. However, the diffusion coefficients for the electrode in the electrolyte with thiourea are slightly larger at the early stage of reduction. The proton diffusion within the carbon interlayer is driven by the gradient of the chemical potential in the near surface region. Under Langmuir conditions of adsorption of H and poison, the chemical potential of H at a given coverage would not be changed by the presence of poison if the poison−H interaction was not considered.[7] During the reduction, even though the catalyst poisons reduce the factional coverage of adsorbed H, the H insertion into the electrode actually is enhanced. Despite the decrease of the total surface H concentration, the concentration of H that will insert into the carbon interlayer may be increased because of the inhibition of the hydrogen recombination process by catalytic poison. Thus, the proton diffusion into carbon interlayer would accelerate. As shown in Figures 7 and 8, the reductions of both R_{ct} and CPE-T during the oxidation process could be explained as that thiourea is desorbed from the surface after being oxidized. After the absorbed thiourea becomes oxidized and subsequently departs from the surface of the carbon, new active sites are created for the oxidation of H, which will enhance the diffusion of H to the surface. The experimental evidence is consistent with the hypothesis. As shown in part B of Figure 9, the diffusion coefficient for the electrode in the electrolyte with thiourea is substantially higher than the one in the electrolyte without the catalytic poison. In summary, even though H under potential deposition (UPD) on the electrode surface is largely suppressed by the competitive adsorption of HS^-, the chemisorbed S species may strongly adsorb on the electrode's surface but become electrochemically desorbed at the oxidation overpotential. This characteristic provides an advantage for using poison catalysts in hydrogen storage or as a hydrogen storage anode because the strong surface adsorption of the poison species could significantly reduce self-discharge or leakage of hydrogen at the reduction potential and with minimum cost to hydrogen oxidation overpotential. As discussed in our previous publication,[3] the carbon interlayer space (d_{002}) plays a great role in the H insertion. It seems that different carbon materials response to the same catalytic poison differently, thus the properties of carbon should influence the phenomenon. Both the carbon structure and surface functionalities could interact with the catalytic poison. More research needs to be done to reveal such an interaction.

Conclusions

The well-known phenomenon that the adsorption of catalyst poisons can promote H electrosorption into metal electrodes is demonstrated on a carbon electrode. The H + H recombination
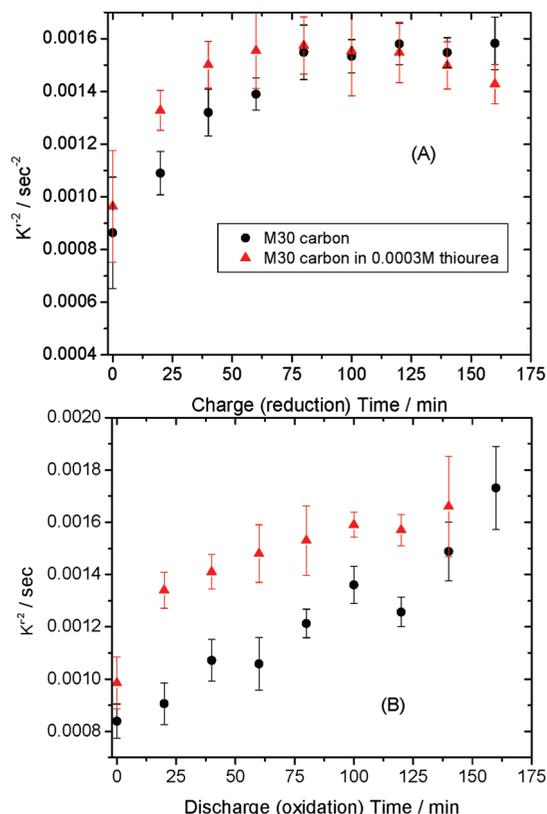
Figure 10. Comparison of the k^{-2}, which is proportional to the proton diffusion coefficient inside the carbon interlayer, for the electrodes in 30% KOH electrolyte with and without thiourea during reduction (A) and oxidation (B). k was obtained by fitting the impedance spectra within 0.001 to 1 Hz.

process on the surface of carbon is believed to be blocked by the chemisorbed thiourea on the carbon surface, enhancing the H insertion into the carbon interlayer.

Through ac impedance and equivalent circuit fitting, it is postulated that the functional groups on the carbon surface can be replaced by thiourea, and the electrosorbed thiourea can become reduced and desorb from the surface of the electrode during oxidation. However, the catalytic poison remains adsorbed during the reduction process. The surface behaviors of thiourea during the electrochemical oxidation and reduction can provide additional benefits. The strongly adsorbed thiourea significantly reduces self-discharge for a fully loaded electrode resting at open circuit potential. After becoming oxidized and departing from the electrode's surface, additional new active sites for H are created, thus improving the H oxidation kinetics.

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