Electrochemical Hydrogen Storage in Amine-Activated Polydopamine

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Electrochemical hydrogen storage combines the evolution, oxidation, and storage of hydrides from aqueous electrolytes and ionic liquids, but presently requires palladium or rare-earth metals to achieve significant power capacities. Here hydrogen electrosorption in amine-activated polydopamine is shown. The organic heterogeneous amine-hydride yields a gravimetric hydrogen density of 0.44%, corresponding to a 80% hydride-per-monomer content, and offers similar reaction kinetics as for palladium and related systems. An initial stability test of 100 electrosorption cycles that demonstrates resilience in acidic media with a tendency for increased capacity over time is included. In situ vibronic amine-hydride fingerprints corroborate the reversibility and stability of the conversion process and highlight the merits of amine-activated polydopamines as a heterogeneous organic hydrogen storage system.

1. Introduction

Safe and low-cost methods for reversible proton-hydrogen conversion are the driving force for powering electric devices based on carbon-neutral energy cycles.[1–5] Electrochemical hydrogen storage consolidates proton-reduction, hydride storage and hydride re-oxidation offering a variety of applications such as rechargeable batteries or electrochemical capacitors.[6–8] However, only few catalytic metals and metal composites, among them palladium and rare-earth metals alloys, show hydrogen electrocatalysis (HES). Hydrogen is thereby chemisorbed as interstitial hydride of type MeH.

We sought to activate amines in conducting polydopamine toward mainly (-DA-) monomers and by that achieved a polymer with mainly primary amines (+NH2) based on prior art synthesis.[44–46,48,49] We reduced the reaction temperature to 150 °C and achieved a polymer with 70% primary amines. This amine-activated polydopamine (aaPDA) showed effective HES similar to palladium with a maximum of the hydrogen capacity close to 0.2 V versus RHE. At higher cathodic potentials, the hydride formation was gradually superseded by hydrogen evolution. We found HES was reversible: The re-oxidation peak occurred at +0.5 V, so that the potential difference between absorption and desorption spanned 0.6 V. This difference was substantially higher as compared to metal-hydrides aiding the system’s resilience against overoxidation. aaPDA achieved a gravimetric hydrogen density equal to PdH0 at 0.44%. This corresponded to 80% of the monomers activated for HES leading to a coulometric capacity of 0.12 Ah g−1. We included an initial stability test with 100 electrosorption cycles and report the continuous activation of aaPDA over time.

In this work, we present a heterogeneous organic amine-hydride system as metal-free alternative. We sought to activate amines in conducting polydopamine for HES to achieve a stable and reversible electrochemical hydride system operating in aqueous media at ambient pressures and temperatures. Earlier works revealed the nature of amines in polydopamines steer the selectivity; indole (and indoline) favored electrocatalytic hydrogen-evolution, while primary amines, such as the dopamine (-DA) building block, possessed large binding energies for as-reduced hydrogen.[46] From that we hypothesized that (primary) amine-activation in polydopamine led to hydrogen electrosorption.

We subsequently modified the structure of polydopamine toward mainly (-DA)n monomers and by that achieved a polymer with mainly primary amines (+NH2) based on prior art synthesis.[46–48,49] We reduced the reaction temperature of the oxidative chemical vapor deposition (OCVD) polymerization to 150 °C and achieved a polymer with 70% primary amines. This amine-activated polydopamine (aaPDA) showed effective HES similar to palladium with a maximum of the hydrogen capacity close to ∼0.2 V versus RHE. At higher cathodic potentials, the hydride formation was gradually superseded by hydrogen evolution. We found HES was reversible: The re-oxidation peak occurred at +0.5 V, so that the potential difference between absorption and desorption spanned 0.6 V. This difference was substantially higher as compared to metal-hydrides aiding the system’s resilience against overoxidation. aaPDA achieved a gravimetric hydrogen density equal to PdH0 at 0.44%. This corresponded to 80% of the monomers activated for HES leading to a coulometric capacity of 0.12 Ah g−1. We included an initial stability test with 100 electrosorption cycles and report the continuous activation of aaPDA over time.
These results were supported by in situ vibration spectro-electrochemistry revealing signature features of rising NH-vibrations upon electrochemical reduction. We concluded with discussing heterogeneous amine-hydrogen storage as important step toward using hydrogen as energy carrier without requiring the evolution of molecular $\text{H}_2$.

2. Results and Discussion

Amines in conducting polydopamine were shown to steer electrocatalytic selectivity in different directions (Figure 1): Secondary amines, such as in the condensed indoline and indole-fragments, implement hydrogen evolution reaction (HER).[46–48] Primary amines, such as present in the dopamine (-DA)$_n$ building block, possessed too high binding energies so that they suppress the hydrogen evolution but therefore enable hydrogen electrosorption (HES).

We found it attractive to harness electrocatalytic amines in dopamine for a heterogeneous amine-hydride with the aim to substitute classic $\text{PdH}_x$ and related metal composite systems. For this, we synthesized amine-activated polydopamine (aaPDA) based on earlier experiments (Figure 1a): We referred to oxidative chemical vapor deposition (oCVD) polymerization using dopamine as educt monomer.[45] We modified the oCVD in the sense to reduce the temperature in the reaction zone to maximum 150 °C to balance the oxidation power and to favor the direct oxidative polymerization (and doping) of dopamine, whilst suppressing its unwanted oxidation to i) dopaminequinone or ii) leucodopaminechrome and 5,6-dihydroxyindole. Such quenching of the reaction temperatures to 150 °C, more than 50% compared to the vaporization temperature at 320 °C, led to dopamine (-DA)$_n$, as the main building block to result as aaPDA (Figure 1a): we achieved an average ratio of 7:3 between primary amines (NH$_2$ from dopamine and dopaminequinone) and secondary amines (–NH- from indoline and indole derivatives) indicated by the high resolution scan of the N1s XPS pattern (Figure 1b). We also resolved the O1s pattern with a ratio of 2.6:1 between hydroxy- to quinone that similarly pointed at a suppressed quinoid formation (Figure 1c). Further, the O1s patterns indicated a maintained doping ratio (monomer:bisulfate, here reported at 3.2:1 (i.e., more than every third monomer doped); the latter corresponded to conducting polydopamines and other related conducting polymers.[49–51]

Based on the presence of 70% primary amines, the aaPDA possessed electrosorption-selective hydrogen-bonds from primary amines in combination with adjacent hydroxy- and keto-groups, along the entire electrically conducting backbone. These functions acted as the hydride formation centers with a theoretical maximum capacity of one proton per monomer (Figure 1d). To study HES, we deposited the aaPDA directly on carbon, which served as inert carrier electrode. The electrochemical characterization included cyclic voltammogram and chronoamperometric/chronocoulometric scans as well as spectroelectrochemical in situ ATR-FTIR (electrochemical-induced absorption, EIA). We consistently used 1 M trifluoromethanesulfonic acid (TFOH, pH = 0) as the electrolyte at 25 °C and 1 atm. This specific electrolyte acted as inert proton source. We referred all electrochemical data versus the reversible hydrogen electrode (RHE, pH = 0). Fingerprint feature of HES in the cyclic voltammogram was the steep rise of the electric Faraday current starting at an electrochemical underpotential versus RHE. The steep rise peaked at −0.2 V versus RHE, where quantitative amounts of hydrogen were electrosorbed (Figure 2a). By sweeping further to the negative, the current decreased to a local minimum at −0.4 V versus RHE. Beyond this potential, the current rose again and hydrogen evolution was observed (steep exponential rise of the current). In the reverse scan, the voltammogram showed a flattened profile coinciding to an isosbestic point at +0.2 V versus RHE. At +0.51 V, we observed the maximum of the re-oxidation peak of the electrosorbed hydride to the proton. The forward-scan showed also an isosbestic point at an similar potential around +0.2 V.

The cyclic voltammograms (CVs, 100 consecutive scans) exhibited reversible electrosorption including ab- and desorption peaks with a potential difference of average 0.6 V (Figure 2a). The peak currents increased gradually by repeating number of cycles, which we assigned to a change of the local pH in the vicinity of the electrode paired with a continuous slight activation of aaPDA. The presence of isobestic points in forward and back-scans (+0.2 V vs RHE) provided evidence that the electrosorption progressed without notable side reactions. These results demonstrated the reversibility of the aaPDA as electrosorptive electrode. The potential difference aided the resilience of amine-hydrides as compared to metals (with characteristic only 0.15 V).[51] In addition, we used chronocoulometry to show the dynamics of electron and proton transfer measured at the maxima of absorption and desorption (−0.2 V and +0.51 V vs RHE, respectively, Figure 2b). For absorption two characteristic regimes were observed: a fast capacitive and slower diffusion-controlled regime with different reaction constants. For desorption, we subtracted the capacitive baseline currents as these were substantial. From chronocoulometry we derived the reaction rates $k_{\text{red/ox}}$ for reduction 0.034 and re-oxidation 0.018 s$^{-1}$ corresponding to 30–50 s (linear fit in Figure S1, Supporting Information). According to that, we found a gravimetric hydrogen storage capability close to 80% electrosorbed hydrogen per monomer within 30–50 s ($k_{\text{red/ox}}$). This corresponded to a power capacity of 0.120 Ah g$^{-1}$ or a gravimetric hydrogen density $\omega_H$ of 0.44% (Equations (1) and (2)). The theoretic limit for hydrogen storage in aaPDA corresponds to 1 proton per monomer (1 amine in (-DA)$_n$), $\omega_H$ equals 0.56%.

$$\omega_H = \frac{0.8 \times M_{\text{H}}} {M_{\text{aaPDA}}}$$

$$M_{\text{aaPDA}} = M_{(-\text{DA})_n} + \frac{M_{\text{H}2\text{SO}_4}} {3.2} = 181.5 \text{ g mol}^{-1}$$

The factor 3.2 accounted to the ratio between the monomer (-DA) and bisulfate (H$\text{SO}_4^-$) as derived from the XPS-scans (3.2:1 corresponds to the frequently observed Coulomb limit of conducting polymers, Figure 1c).[51]

Further chronoamperometric scans were recorded at different electrosorption potentials that revealed a similar charge (and proton) dynamics: We varied the potentials close to RHE = 0 (absorption) (Figure 3a) and at the desorption peak around +0.5 V versus RHE, respectively (Figure 3b). These
results corroborate the characteristic 2-regime dynamics earlier reported in PdH with capacitive and diffusion-controlled regimes indicated by the steep decay and subsequent saturation or slight decrease of the current. From that, we derived the potentiocoulometry for the initial electrosorption regime (integrated first 10 s) that shows the immediate charging occurring to up to 80% capacity protons per monomer, \((-DA\)\)\(_{n}\) (Figure 3c,d). In these scans we considered the upper and lower

Figure 1. Structure of oxidative CVD-synthesized amine-activated polydopamine: a) 150 °C synthesis path favoring i) direct polymerization and suppressing, ii) intermediate side-oxidation to the corresponding quinone or indoline (and indol) to result amine-activated polydopamine (aaPDA). b) N1s XPS high-resolution XPS revealed the ratio is 7:3 between primary (dopamine) amines and secondary (indoline and indole) amines. c) O1s high-resolution XPS revealed 55% of oxygen from bisulfate yielding a monomer:sulfate ratio of 3.2:1 (doping concentration). Further it showed a 3:1 ratio between dopamine:quinone, i.e. 38% of hydroxy-groups reacted to the corresponding quinoid form. d) Electrosorption reaction mechanism: amine-activated aaPDA can take up to one proton per monomer. The mechanism suggested the formation of an additional N–H bond.
potential limits, for reduction higher than $-0.34 \text{ V versus RHE}$ (hydrogen evolution) and for re-oxidation beyond $+0.8 \text{ V versus RHE}$ (oxidation of polymer). For qualitative analysis of the intermediately formed amine-hydrides we used electrochemical-induced absorption spectroscopy (EIA) in the infrared. The study probed vibronic changes during proton reduction/re-oxidation. We therefore installed a 2-electrode configuration without liquid electrolyte, in order to reduce the spectral background noise (Figure S2, Supporting Information): we applied a (solution-processed) proton membrane between aaPDA and an inert platinum counter electrode. aaPDA was deposited on germanium (Figure 4a) serving as carrier electrode and ATR element. With that, we studied HES by linear sweep voltammetry and in situ ATR-FTIR. The reference potentials were determined by the current-voltage scans using reduction- and re-oxidation peaks as well as the local minima at the isosbestic points ($+0.2 \text{ V vs RHE}$, Figure 4a, inset). From that we scanned multiple spectra ($T_{min}$, $T_{max}$) at $+0.2 \text{ V versus RHE}$ (current minima) and at $-0.2 \text{ V versus RHE}$ (maximum of absorption) and referenced them against the baseline reference scan.

Figure 2. Cyclic voltammogram and charge balance: a) Gravimetric current density $j$ showed reversible hydrogen electrosorption (HES) with negative reduction peak at $-0.24 \text{ V}$, positive re-oxidation peak at $+0.54 \text{ V}$ and the isobestic point minima at $+0.2 \text{ V}$. The cyclic voltammogram (50 mV s$^{-1}$) revealed a rising electrosorption current with repeating number of cycles. b) Chronocoulometric scans at the reduction and re-oxidation peak maxima indicated the proton-to-hydride reaction constants reaching 0.8 protons per monomer after 20 s.

Figure 3. Electrodynamics of HES: a) Chronoamperometry shows the absorption of protons in aaPDA at increasing potentials from 0 to $-0.34 \text{ V versus RHE}$. b) Corresponding decharging chronoamperometry at potentials from $+0.26$ to $+0.61 \text{ V versus RHE}$. c) Integrated charge per dopamine monomer, (-DA)$_n^-$, for the absorption and d) desorption process.
3. Experimental Section

Synthesis and Characterization: Amine-activated polydopamine (aaPDA) was synthesized by oxidative chemical vapor deposition (oCVD) from dopamine hydrochloride and sulfuric acid according to Coskun et al. with a modified reactor: A long quenching path of 20 cm was inserted between vaporization-zone (dopamine and sulfuric acid, 320 °C) and reaction (and deposition) zone, which remained unheated. By that the temperature in the reaction zone (close to the substrate) was leveled to a maximum 150 °C.

aaPDA was deposited on carbon felt (CF) (10 mm × 10 mm) (SGL Group, The Carbon Company, SEM before and after electrosorption in Figure S10, Supporting Information) and, for spectroelectrochemistry, on germanium. Prior deposition of the active layer, all substrates are cleaned using ultrasonic bath 15 min each in acetone, isopropyl alcohol, Hellmanex-detergent (Hellma, 70 °C) and deionized water. Before starting the synthesis, dopamine hydrochloride (Sigma-Aldrich) was dried in the oven at 150 °C overnight in presence of CaH2 (95%, Sigma-Aldrich) to remove any water residual. The reaction was carried out in a tube furnace (Carbolite company; glass tube length: 45 cm; tube diameter: 2.4 cm) at a vaporization temperature of 320 °C under nitrogen atmosphere with a carrier gas-flow of 3 L min⁻¹. Sulfuric acid (95–97%, J.T. Baker) and sodium sulfate (≥99.0%, Sigma-Aldrich) are used as oxidation agent and corresponding salt, to enhance the balance toward SO3⁻ and SO4²⁻ in the gas phase. The chemical composition of aaPDA was determined by X-ray photoelectron spectroscopy (XPS). All measurements were recorded on aaPDA directly deposited on carbon felt electrodes. A Theta Probe from ThermoFisher Scientific was applied with an Al Kα (1486.7 eV) source. The charge was compensated by a Dual Flood Gun (1-2 eV electrons and Ar⁺ ions), and the lens mode was set to standard. The energy pass amounted to 200 eV for the survey scan and to 50 eV for high-resolution (HR) scans, with energy steps of 1 and 0.1 eV, respectively. For data analysis, the Avantage v5.32 software package was used. The data fittings were in agreement with results described in the literature. The elemental concentrations were determined by survey and HR scans shown in Figure 1b,c (NTs and O1s) as well as in Supporting Information (spectral survey scan, CTs, S2p, Figures S4–S6 and NTs, S2p and F1s as-deposited, before and after hydrogen electrosorption, Figures S8–S9, Supporting Information).

Electrochemical Characterization: Electrochemical experiments were carried out using a JAI SSEL Potentiostat Galvanostat IMP 88 PC. To examine amine-activated polydopamine (aaPDA) in HES, electrochemical studies were conducted in a standard three-electrode arrangement in an H-cell configuration (separated cathode space). A PDA-coated carbon felt (CF) (10 mm × 10 mm) was used as a working electrode (WE), Pt as a counter electrode (CE), and Ag/AgCl (3 M KCl) as a reference electrode (RE, +0.197 V vs the standard hydrogen electrode, SHE). All experiments (except those related to spectroelectrochemistry) were carried out in a 1 M trifluoromethanesulfonic acid (TOH, pH = 0) as the electrolyte solution at 25 °C. The compartments were connected by a bridge using glass frit (porosity No. 2). All results reported were calculated versus the reversible hydrogen electrode (vs RHE equal to SHE at pH = 0) scan rates of 50 and 5 mV s⁻¹ (Figure S12, Supporting Information). For comparison, a CV
was included in 1 M HCl as alternative electrolyte (Figure S1, Supporting Information). The cell constants were characterized by electrochemical impedance spectroscopy (EIS) using an IVIUM compactstat (The Netherlands). At the open circuit potential (OCP) the impedance spectra were recorded in the range from $10^{-1}$ to $10^{4}$ Hz with a perturbation amplitude of 50 mV in standard electrode configurations (Pt-Pt, Pt-CF, Pt-CF-aaPDA, Figure S3 and Table S1, Supporting Information).

**Spectroelectrochemistry:** Electrochemical-induced absorption (EIA) was recorded in situ using internal reflection mode attenuated total reflection (ATR) - FTIR. The measurements were performed on a Bruker IFS 66/S Spectrometer. The in situ specimen consists of a germanium ATR element (parallelipped, $1 \times 10.5 \times 45$ mm, 45°). Harrick Scientific Products Inc.), which co-served as working electrode carrier. On top aaPDA (working electrode, WE) and a Pt counter electrode (CE) resembling a 2-electrode electrochemical cell (Figure 4a) were deposited. As electrolyte, an activated proton membrane was used (Nafion 117, Sigma-Aldrich, SEM picture in Figure S7, Supporting Information), which was deposited by drop casting from solution onto aaPDA/germanium. EIA was recorded by recording from reference spectra (without bias, $T_{0}$) and biased spectra at two potentials: one at the maximum of the electrosorption peak (corresponding to $T_{\text{max}}$) and one at the onset of electrosorption (corresponding to $T_{\text{min}}$). The potentials were referenced to the isosbestic point at $0.2$ V versus RHE (minimum of current) from the curren–voltage scans of the 2-electrode cell (inset in Figure 4a). To improve the signal-to-noise, the measurements were repeated 100 times (noise level shown in Figure S2, Supporting Information). EIA spectra were then calculated by subtracting (and normalizing) the accumulated reference and bias scans according to Equation (3).

$$\frac{\Delta T}{T} = \frac{T_{\text{max}} - T_{\text{min}}}{T_{0}} = -\ln(T) = A$$

(3)

The spectra ($-\Delta T/T$) showed the differential absorption induced by electrochemical bias. The positive spectral vibration features correspond to bonds formed by electrosorption.

**Supporting Information**
Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**
The authors declare no conflict of interest.

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