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Electrochemical reductive biomass conversion: direct conversion of 5-hydroxymethylfurfural (HMF) to 2,5-hexanedione (HD) *via* reductive ring-opening[†]

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2,5-Hexanedione (HD), which can be produced by reduction of 5-hydroxymethylfurfural (HMF), one of the most important biomass intermediates, can serve as a precursor to produce various biofuels and key building block chemicals. The conversion of HMF to HD requires reduction of both the alcohol and aldehyde groups to alkane groups as well as opening of the furan ring. In this study, a direct electrochemical conversion of HMF to HD at ambient pressure and temperature was demonstrated without using H₂ or precious metal catalysts. Water was used as the hydrogen source and zinc was used as the catalytic electrode, which enabled hydrogenolysis and Clemmensen reduction coupled with furan ring opening. Optimum conditions to achieve high Faradaic efficiency (FE) and selectivity for HD production were investigated and plausible mechanisms were proposed. The environmentally benign one-step procedure to produce HD reported in this study will serve as a new route to valorize biomass intermediates.

Increasing concern over petroleum supply and climate change has driven the search for viable alternatives for our chemical and transportation fuel needs. Biomass has emerged as a leading contender due to its renewable nature and the vast number of compounds it can be used to generate, many of which have similar or improved properties to their petroleum based counterparts.¹⁻¹² 5-Hydroxymethylfurfural (HMF) has become one of the most important biomass intermediates. Derived from cellulosic matter, the most abundant organic material on earth, HMF can be processed to a wide variety of important chemicals including transportation fuels (internal combustion, compression ignition, and jet engines), polymers, and pharmaceuticals.^{1–15} Alternative transportation fuels have been of particular interest in recent years, with ethanol filling that role as a first generation biofuel. Concerns over its low energy content, high water solubility, and competition with

food supply, among others, have led to the search for next generation biofuels.^{9,10} 2,5-Dimethylfuran (DMF) is one possible candidate. Traditional production of DMF has proceeded *via* hydrogenation and hydrogenolysis of HMF under high temperatures (393–573 K) and pressures of H₂ (6.8–62 bar).^{9,10,16} DMF has a high octane number (119) and 40% higher energy content than ethanol, similar to gasoline, while immiscible with water.^{9,10}

Another alternative-fuel candidate is methylcyclopentane, which has a higher octane number and higher energy content than gasoline, and has fewer toxicity concerns than DMF.¹¹ It was recently demonstrated that methylcyclopentane can be produced from 2,5-hexanedione (HD), which is a hydrated form of DMF, by base-catalyzed intramolecular aldol condensation to 3-methylcyclopent-2-enone (MCP) followed by reduction (Fig. 1a).¹¹ Aside from applications in alternative-fuels, HD can also be used to produce *para*-xylene, an important precursor in the production of terephthalic acid for poly-ethylene terephthalate (PET) (Fig. 1a).¹² In addition, HD can



Fig. 1 (a) Conventional production and potential use of HD and (b) direct electrochemical reduction of HMF to HD enabled by this study.

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[†]Electronic supplementary information (ESI) available: NMR data of the products, SEM of Zn electrodes, and proposed mechanisms for the electrochemical reduction of HMF to HD and HMF to HHD. See DOI: 10.1039/c6gc00533k

be further reduced to 2,5-hexanediol, which has applications in polymer synthesis, or to hexane (Fig. 1a). This suggests that HD is a critical and versatile intermediate to form biofuels and building block chemicals.

To date, conversion of HMF to HD has been achieved by reduction of HMF to DMF using precious metal catalysts and H₂ gas at high temperature and pressure, followed by ring opening via hydration (Fig. 1a).^{11,16,17} Here, we report the direct electrochemical reduction of HMF to HD using zinc as the catalytic electrode at ambient temperature and pressure (Fig. 1b). This process does not require the use of H_2 gas or precious metals. Water (i.e. protons) is used as the hydrogen source without pre-reducing water to H₂ and HMF is directly converted to HD on the electrode surface without producing DMF. A few studies on electrochemical reduction of HMF or furfural have been reported previously with the reduction of aldehyde group to alcohol being the most commonly observed reaction.¹⁸⁻²⁶ However, this study represents the first example of electrochemical reductive ring-opening of HMF with complete reduction of both the alcohol and the aldehyde groups.

The unique catalytic ability of Zn for electrochemical reduction of HMF to HD was first examined by comparing its linear sweep voltammograms (LSV) for HMF reduction with those of Au, Cu, and Pt (Fig. 2). For electrochemical reduction of HMF in aqueous media, water reduction to H_2 is the major competing reaction. Therefore, identifying good HMF reduction catalysts among poor H_2 evolution catalysts is necessary for achieving high Faradaic efficiency (FE) for HMF reduction. Au and Cu were chosen as poor H_2 evolution catalyst to compare with the performance of Zn for HMF reduction.

LSVs were performed in a 0.2 M sulfate buffer solution (pH 2.0) with and without 0.02 M HMF in an undivided three-



Fig. 2 LSVs of (a) Pt, (b) Au, (c) Cu and (d) Zn electrodes in 0.2 M sulfate buffer (pH 2.0) with (red) and without (black) 0.02 M HMF (scan rate: 50 mV s^{-1}).

electrode cell without stirring. The cathodic current shown in LSVs obtained before HMF was added is due to water reduction to H_2 . As expected, Pt showed the most positive onset, followed by Au, Cu, and Zn. When HMF was added, Pt did not show a change either in the onset potential or in current profile, because water reduction is dominant on the Pt surface whether or not HMF is present. In the case of Au and Cu, the onset potential for reduction current was shifted to the positive direction by 50–100 mV when HMF was present, suggesting HMF reduction occurs before H_2 evolution on these electrodes. The most significant change in onset potential and current profile when HMF was added was observed for Zn, which demonstrated a current density of more than 4 mA cm⁻² for HMF reduction at the potential where water reduction initiates.

The reduction products and conversion efficiencies for HMF reduction were analyzed by performing HMF reduction in a divided cell at a constant potential of -1.2 V vs. Ag/AgCl (equivalent to -0.89 V vs. RHE) by passing 20 C in 14 mL of a 0.2 M sulfate buffer solution (pH 2.0) containing 0.02 M HMF. It should be noted that the reduction of HMF to HD consumes protons (Fig. 1b). Therefore, the local pH at the working electrode will rapidly rise during the course of electrolysis if an unbuffered weakly acidic solution is used. This pH change can constantly vary the yield, selectivity, and the type of product throughout the electrolysis. Therefore, in order to accurately evaluate the pH effect, it is critical to use a buffered solution to obtain results at a constant pH of interest. After reduction, the electrolyte was analyzed by ¹H-NMR to quantify the products (Fig. S1[†]). Based on these results, FE and selectivity for HD formation were calculated using the following equations (eqn (1) and (2)), where F is the Faraday constant (96 485 C mol⁻¹) and n is the number of electrons required for the conversion of an HMF molecule to an HD molecule, which is 6. The results are summarized in Table 1.

$$FE(\%) = \frac{\text{mol of HD formed}}{\text{Total charge passed } (C)/(F \times n)} \times 100\%$$
 (1)

Selectivity of $HD(\%) = \frac{\text{mol of HD formed}}{\text{mol of HMF consumed}} \times 100\%$ (2)

Table 1 Electrochemical HMF reduction by Pt, Au, Cu and Zn $electrodes^a$

Electrode	Pt	Au	Cu	Zn	
Average current density (mA cm $^{-2}$)	57.4	50.1	39.6	14.4	
HMF consumed (µmol)	5.01	11.9	16.0	30.6	
HD formed (µmol)	0	0.826	1.30	25.0	
BHMF formed (µmol)	5.00	5.10	6.32	0.978	
HHD formed (µmol)	0	0.823	1.98	2.75	
FE for HD(%)	0	2.39	3.75	72.4	
Selectivity for HD(%)	0	6.92	8.13	81.6	
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^{*a*} Reaction conditions: E = -1.2 V vs. Ag/AgCl (= -0.89 V vs. RHE) in a 0.2 M sulfate buffer (pH 2.0) containing 0.02 M HMF for 20 C passed.

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As expected, H_2 production was the major reaction on Pt; only a small amount of HMF was converted to 2,5-bis(hydroxymethyl)furan (BHMF) (FE = 4.83%) and no HD was detected. In the case of Au and Cu, a slightly larger fraction of charges were used for BHMF production (FE = 4.92% and 6.10% for Au and Cu, respectively). HD was also detected as a reduction product, but FE for HD production was below 4%. Surprisingly, Zn electrodes produced HD at high efficiency (FE = 72.4%) and selectivity (81.6%) with only a trace amount of BHMF (FE < 1%). Hydroxy-2,5-hexanedione (HHD) was also detected as a byproduct (FE = 5.64%). The reduction of HMF to BHMF, HD, and HHD requires 2e⁻, 6e⁻, and 4e⁻, respectively as the reaction schemes show in Fig. 3a. DMF was not detected, suggesting that the electrochemical conversion of HMF to HD does not involve the formation of DMF.

The potential dependence of HD production by Zn in the same solution was investigated and the results are summarized in Table 2. The highest FE (72.4%) was achieved at -1.2 V vs. Ag/AgCl. Applying more negative potentials (E < -1.4 V vs. Ag/AgCl) decreased FE for HD production because water reduction became more favorable on the Zn surface in the high overpotential region. When a more positive potential than -1.2 V was applied, FE did not change significantly, but the average current decreased, which decreased the rate for HD production.

The conversion of HMF to HD on Zn demonstrates a strong dependence on solution pH. When the pH of the sulfate solution was lowered to 1, HD was still produced but the FE for HD production decreased (FE = 50.7% at -1.2 V vs. Ag/AgCl) because water reduction became more favorable at a lower pH.



Fig. 3 Electrochemical reduction products of (a) HMF and (b) 5-MF on Zn at -1.2 V vs. Ag/AgCl in a 0.2 M sulfate buffer solution (pH 2.0) containing 0.02 M HMF.

Table 2	Electrochemical	HMF	reduction	by	Zn at	t various	potentials ^a
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$E(V) \nu s. Ag/AgCl$	-1.0	-1.2	-1.4	-1.6
Average current density (mA cm ⁻²)	6.27	14.4	20.4	39.2
HD formed (µmol)	23.4	25.0	22.7	12.9
FE (%)	67.6	72.4	65.8	37.4
Selectivity (%)	77.6	81.6	79.5	60.6

 a Reaction conditions: 0.2 M sulfate buffer (pH 2.0) containing 0.02 M HMF for 20 C passed.

On the other hand, when the pH was increased to 7.2 (0.2 M phosphate buffer), no HD was formed and the major product was BHMF (57.7% FE at -1.7 V vs. Ag/AgCl). We confirmed that this is truly due to the pH effect and not due to the anion effect (phosphate vs. sulfate) by performing the same reduction reaction in a pH 2.0 solution using a phosphate buffer, which produced HD at efficiencies that were equivalent to those in sulfate (pH 2.0). When a midpoint pH was tested using a 0.2 M acetate buffer (pH 4.7), HD was still formed but the FE dropped to 28% at -1.2 V vs. Ag/AgCl along with a corresponding increase in the production of BHMF. Therefore, pH 2 was identified as an optimum pH to produce HD.

Since HD is a hydrated open ring structure of DMF, the conversion of HMF to HD is in essence composed of three steps: hydrogenolysis (*i.e.* replacement of the alcohol group with a terminal hydrogen), the conversion of the formyl group to a terminal alkane, and ring opening. We believe that the unique ability of Zn to produce HD by HMF reduction is related to the well-known ability of Zn to perform the Clemmensen reduction, which reduces aldehydes or ketones to the corresponding hydrocarbon, consuming 4 protons and 4 electrons with a removal of one H_2O (Fig. 4a).²⁷

The fact that DMF was not detected as a byproduct or an intermediate suggests that for electrochemical HMF reduction on Zn in an acidic medium, the formation of DMF and the hydrolysis of DMF to HD do not occur in a decoupled sequential manner. Rather, acid catalyzed ring opening of a furan ring and Clemmensen reduction occur in a concerted manner, resulting in direct reductive ring opening of HMF to HD. However, the mechanism for opening of the furan ring should still be similar to those well established for other furan rings, which commonly involve the ring opening between C2 and the furan oxygen by a nucleophilic attack from water.^{28–30} The ring



Fig. 4 (a) A general mechanism of Clemmensen reduction on Zn. Zn is used as the electron source and the (+) charges on Zn represent how many electrons are used in each step; (b) a ring-opening mechanism of DMF to HD by hydrolysis; (c) a predictive model for the reduction of 5-MF to HD constructed by combining mechanisms shown in (a) and (b).

opening of DMF to HD is shown in Fig. 4b as an example.³⁰ Consequently, one carbonyl oxygen of HD is from the furan oxygen and the other carbonyl oxygen is from water.

A key remaining question in proposing a mechanism for the reduction of HMF to HD is when the hydrogenolysis of HMF occurs (*e.g.* before, during, or after Clemmensen reduction). In order to examine whether the hydrogenolysis step of HMF is critical for reductive ring opening, we performed the reduction of 5-methylfurfural (5-MF) on Zn using the same reduction conditions (Fig. 3b). 5-MF is an analogous compound of HMF having a furan ring and a formyl group, but without an alcohol group. The result shows that the same HD was obtained as the only detectable HMF reduction product (FE = 38.3%). The fact that the absence of the alcohol group does not affect the reductive ring-opening process of the furan ring suggests that the hydrogenolysis of HMF to 5-MF is an independent step from reductive ring opening and it most likely occurs before reductive ring opening.

By combining Clemmensen reduction and ring-opening mechanisms, a predictive model for the reduction of 5-MF to HD on the Zn surface is proposed in Fig. 4c. The resemblance of the predictive model to Clemmensen reduction and ringopening mechanisms can be easily seen by comparing Fig. 4c with Fig. 4a and b, where Steps 1, 2, 3, and 7 are associated with Clemmensen reduction while steps 4-6 are associated with ring opening. As in the case of the conversion of DMF to HD, one carbonyl oxygen of HD is from the furan oxygen of 5-MF and the other carbonyl oxygen is from water while the formyl group of 5-MF is converted to the terminal alkyl group by Clemmensen reduction. In the conventional Clemmensen reduction Zn serves as the electron source and is oxidized to Zn²⁺. However, in our electrochemical cell, electrons are provided from the half reaction occurring at the anode (water oxidation). Therefore, the catalytic surface of Zn is not oxidized during the reduction process. Scanning electron microscopy (SEM) images of the Zn electrode before and after the HMF reduction are shown in Fig. S2.† After HMF reduction, the Zn surface was roughened, suggesting that the Zn surface was restructured during the catalytic reaction by HMF-Zn interactions. However, after initial restructuring, no further alteration of the Zn surface was observed when the reduction was prolonged.

A plausible mechanism for the reduction of HMF to HD is also shown in Fig. S3[†] where hydrogenolysis of HMF precedes ring opening and the remaining reduction steps are exactly the same as those shown for the reduction of 5-MF. As mentioned earlier, HMF reduction also produced a small amount of HHD, which was not detected from reduction of 5-MF. This can be explained by the possibility that a small fraction of HMF goes through reductive ring opening without going through hydrogenolysis first. A plausible mechanism for this pathway is also shown in Fig. S3.[†] In this case, the final ringopened product, HHD, would still contain the alcohol group from HMF. While the conversion of HMF to HD requires 6 electrons and 6 protons with a loss of one H₂O, the conversion of 5-MF to HD and the conversion of HMF to HHD, which do not involve hydrogenolysis, both require only 4 electrons and 4 protons. The relationship between the reduction processes of these three reactions are demonstrated in Fig. S3.†

In summary, we demonstrated that Zn electrodes have the unique ability to electrochemically convert HMF to HD in acidic aqueous media under ambient condition using only water as the H source. The overall reaction is composed of hydrogenolysis and Clemmensen reduction coupled with furan ring opening. FE and selectivity as high as 72.4% and 81.6%, respectively, were achieved for HMF reduction at -1.2 V *vs*. Ag/AgCl in a pH 2 solution, which was an optimal condition to suppress H₂ evolution and the conversion of HMF to BHMF. Comparing the reduction of HMF and 5-MF on Zn, a plausible mechanism for the formation of HD and HHD were proposed. The unique reduction pathway that can directly convert HMF or 5-MF to HD reported in this study will serve as a new route to valorize biomass intermediates.

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