Polyoxometalate-Mediated Lignin Oxidation for Efficient Enzymatic Production of Sugars and Generation of Electricity from Lignocellulosic Biomass

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Conversion of lignocellulosic biomass to various renewable fuels, chemicals, materials, and electricity has attracted more and more interest in recent decades to decrease the dependence on fossil resources and reduce net CO_2 emissions. Herein, we have developed an integrated process of biomass pretreatment for enzymatic hydrolysis of cellulose coupled with electricity generation with polyoxometalates (POMs) and ferric ion as electron mediators and proton carriers. The pretreatment is a "charging" process, and the re-oxidation of the POMs is effectively a "discharging" process. The pretreated substrate showed a good enzymatic digestibility (≈80% cellulose conversion) within a short incubation period (<24 h). Fe^{3+} was screened as a cheap, effective liquid mediator to transfer electrons to air, which is the terminal electron acceptor in the "discharging" process. The highest output power densities of 10.8 and 12.4 mW cm^{-2} were obtained for discharging of reduced $H_3PMo_{12}O_{40}$ and $H_4PMo_{11}VO_{40}$, respectively. This power density is 5000–6000 times higher than that of phenol-fueled microbial fuel cells, and 10 times higher than that of a recently reported direct biomass fuel cell with an air cathode covered with Pt catalyst. Moreover, this work also provides a conceptual combination of a direct biomass fuel cell and a redox flow cell, which can be flexibly switched between electricity generation from biomass and stationary energy storage.

Lignocellulosic biomass, such as agricultural and forest residue, is an abundant renewable feedstock for biofuels production. Typically, agricultural and hardwood lignocellulose contains approximately 30–40% cellulose, 20–30% hemicelluloses, and in the range of 15–25% lignin, whereas softwood lignocellulose contains 40–42% cellulose, 20–30% hemicelluloses, and 25–32% lignin.[1,2] Cellulose and hemicelluloses are carbohydrates and can be used for bioethanol production by enzymatic hydrolysis and microbial fermentation, whereas lignin is usually burnt for heat recovery in a conventional biorefinery. In a typical cellulosic ethanol plant for example, the enzymatic hydrolysis residue, a lignin-rich fraction, is used to produce steam and electricity by steam turbine through combustion in a boiler. This approach of lignin-to-electricity conversion usually has low efficiency due to high exergy loss in combustion.[3] Theoretically, direct conversion of lignin to electricity without external processing always results in low exergy loss. Such direct conversion of lignocellulosic lignin to electricity, however, is challenging because biomass plants have a complex structure that prevents the degradation of its structural components. On the other hand, the cellulose accessibility for enzymatic hydrolysis is greatly limited by the presence of hemicelluloses and lignin.[4,5] Particularly lignin not only functions as a physical barrier to limit the contact of cellulose by cellulase enzymes,[6] but also non-productively adsorb cellulase enzymes.[7] Removing lignin has been proven to dramatically improve the cellulose enzymatic digestibility of lignocelluloses.[8] Lignin can be removed by various chemical processes, among them an oxidative process can substantially modify the lignin structure and decrease surface hydrophobicity that has been known as a main factor for non-productive adsorption of cellulases.[9] However, most of the oxidants used in the oxidative pretreatment, such as O_3, H_2O_2, and $NaClO_2$, are not recyclable or easily regenerated.

Polyoxometalates (POMs) are polyatomic ions consisting of three or more transition metal oxyanions linked together by shared oxygen atoms. They have distinct properties such as robust oxidative degradation ability and acidity, with great potential as electron reservoirs. POMs have been used as catalysts for selective oxidative delignification of pulps using oxygen[10] (Figure 1 A). This is because POMs generally have a higher redox potential than the lignin structures for oxidizing lignin, but lower potentials than oxygen, thereby allowing their possible re-oxidation by oxygen.[10] Based on this principle, Liu et al. developed a solar-induced hybrid fuel cell that can be directly powered with natural polymeric biomasses, such as starch, using polyoxometalates as a photocatalyst and charge carrier to generate electricity at low temperatures.[11] In our previous work, we also achieved efficient conversion of lignin to electricity at 90 °C with an output power density in the range of 0.3–45 mW cm^{-2}, depending on the oxidant used in the cathode.[12] However, when air or oxygen is directly used as the oxidant for discharging, a noble metal cata-

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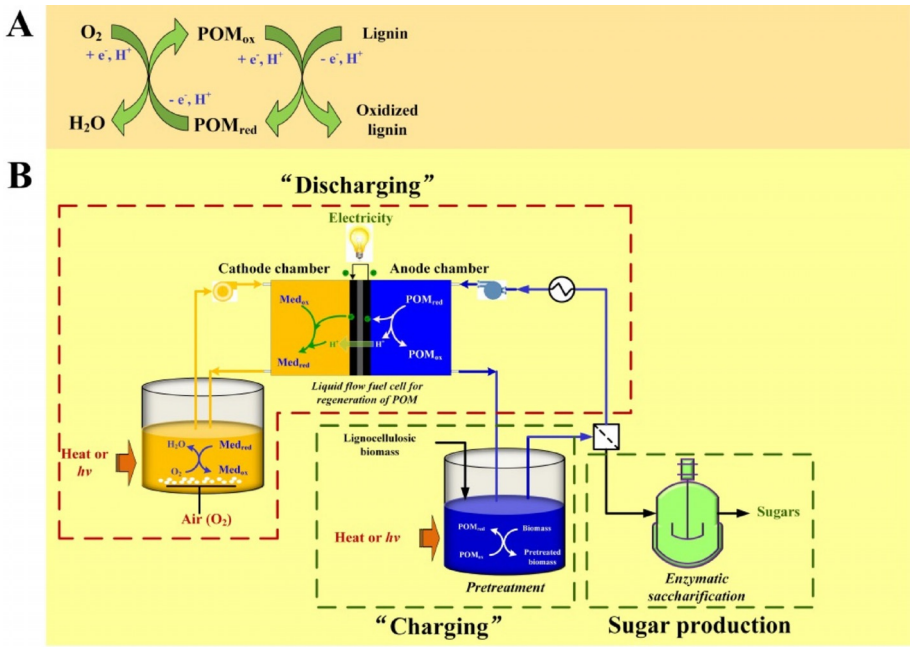

Figure 1. Principle of POM-mediated oxidation of lignin by oxygen (A), and a conceptual integration of biomass pretreatment to increase cellulose digestibility and direct conversion of biomass to electricity mediated by POM (B).

lyst such as Pt has to be used to facilitate the cathodic reaction, and the power density is relatively low. Liquid catalysts such as POMs have been used as the electron mediator in the cathode, which greatly improved the power output.[12,13] However, POMs are relatively expensive, and furthermore, most reduced POMs are not steadily and easily re-oxidized by air under mild conditions. Therefore, it is necessary to find an inexpensive mediator to quickly transfer the electrons released from the reduced POMs of the anode to a low-cost oxidant such as air.

Herein, we have proposed an integrated process mediated by POMs for biomass pretreatment to increase the cellulose digestibility coupled with efficient conversion of the biomass component (especially lignin) to electricity at low temperatures by using a liquid flow cell; this is effectively the conceptual integration of biomass pretreatment coupled with electricity generation (BPCEG, Figure 1B). This conceptual integration can be considered as a modified and updated version of the direct biomass-to-electricity conversion technology with POMs as electron mediators reported recently.[11,12,13] The cell consisted of an anode chamber and cathode chamber separated by a proton exchange membrane (PEM). The anode and cathode chambers were connected to external containers, called anode and cathode vessels, respectively, using silicone tubes (Figure S1, Supporting Information). In the anode vessel, lignocellulosic biomass such as wheat straw was pretreated by POM_{ox} for delignification anaerobically, whereas POM_{ox} was reduced to form reduced POM (POM_{red}). Electrons and protons primarily transferred from the lignin to POM_{ox} as shown in Equation (1). Heat or light can be used to accelerate the reaction. In the anode chamber, the reduced POM_{red} released electrons and protons, and was re-oxidized to form POM_{ox}, which was further recycled to the anode vessel for biomass pretreatment. In the cathode chamber, the mediator (Med_{ox}, such as Fe^{3+} or Cu^{2+}) received electrons to form the reduced mediator (Med_{red}), such as Fe^{2+} or Cu^{+}. In the cathode vessel, the Med_{red} was further re-oxidized to Med_{ox}, achieving transfer of an electron to the final oxidant, such as air (oxygen).

$$\text{lignin-H}_n + \text{POM}_{ox} \rightarrow \text{oxidized lignin} + \text{H}_n\text{-POM}_{red} \quad (1)$$

POM shows very promising properties for biomass pretreatment. First, POM is acidic and can promote the degradation of hemicellulose and fragmentation of lignin; second, POM has oxidizing ability and can capture electrons from lignin and other reductive substances, thereby resulting in oxidative delignification; third, POM can be regenerated by other oxidants with higher redox potentials; fourth, the acidity, oxidizing ability, and redox properties of POMs can be easily tailored by changing the composition of the Keggin units;[14] fifth, POM has photo-induced activity, and thus the pretreatment can be powered by solar energy; and sixth, POM is tolerant to most organic and inorganic contaminants and showed higher stability than noble metal catalysts.[13] Several Keggin-type POMs at a concentration of 0.25 M, including phosphomolybdic acid ($H_3PMo_{12}O_{40}$, PMo_{12}), phosphotungstic acid ($H_3PW_{12}O_{40}$, PW_{12}), and phosphomolybdovanadic acid ($H_4PMo_{11}VO_{40}$, $PMo_{11}V$), were used to pretreat wheat straw by solar (12 h in sunlight without external heating) or heat induction (at 95 °C for 45 min with addition of 0.1 M phosphoric acid, a relatively optimized condition by orthogonal design shown in Table S1, Supporting Information).

The raw wheat straw contained 35.1% cellulose (glucan), 23.4% xylan, 21.1% lignin, 6.8% ash, and 13.6% others. After pretreatment, the dissolution of cellulose, xylan and

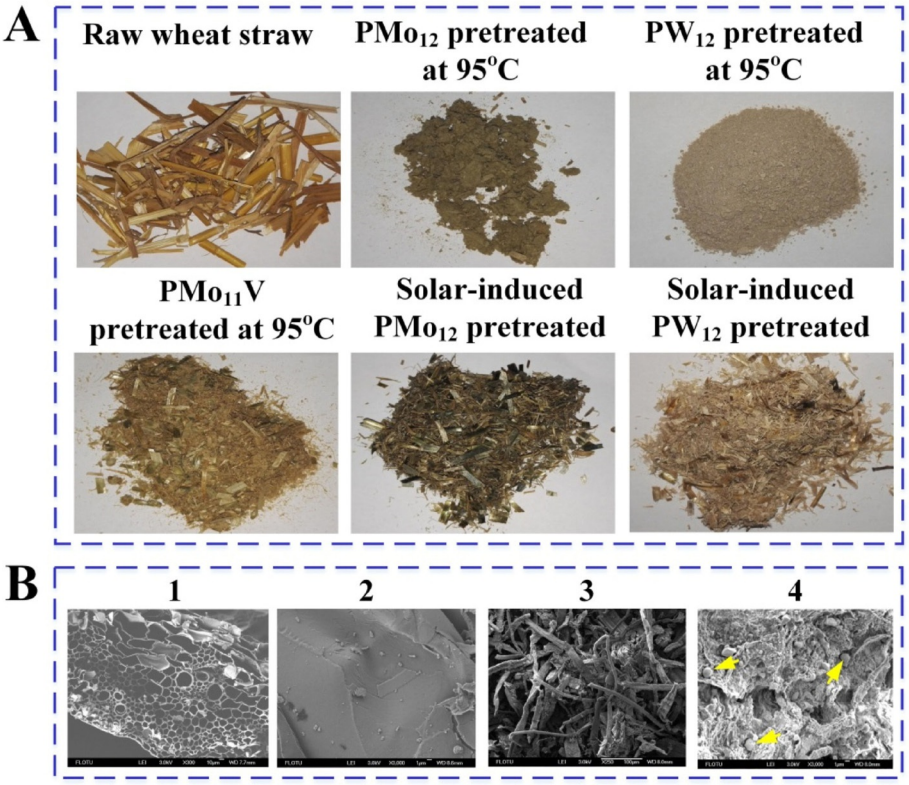

Figure 2. Photographs of raw wheat straw and pretreated solids by different POMs (A), and SEM images of wheat straw structure changes by PMo_{12} pretreatment at 95 °C (B).

lignin were 15–33 %, 33–81 % and 44–72 %, respectively, depending on the POM species and pretreatment condition as shown in Table S1 (Supporting Information). PW_{12} pretreatment obtained a higher degree of delignification and xylan dissolution than PMo_{12} did, whereas $PMo_{11}V$ resulted in the lowest degree of delignification. This is because PW_{12} had the strongest acidity among these three POMs, which was beneficial to xylan hydrolysis and fragmentation of lignin. By POM pretreatment, the wheat straw structure was greatly altered, whereas the heat-induced pretreatment (HIP) showed much more significant changes (Figure 2 A). The wheat straw size shrinks as a result of the solar-induced pretreatment (SIP), and becomes even finer by HIP. Scanning electron microscopy (SEM) images (Figure 2 B) revealed a clear cell wall structure for the raw wheat straw (Figure 2 B1) with compact and non-porous surface morphology (Figure 2 B2). After PMo_{12} pretreatment, the cell wall structure was decomposed to form fine fibers with lengths shorter than 500 μm (Figure 2 B3). The substrate surface became much coarser with porous structure (Figure 2 B4), and therefore the specific surface area was greatly increased; spherical particles were also observed. It was observed that PMo_{12} oxidation may cause acid-catalyzed condensation of lignin to lead to higher molecular weight.[12] Therefore, the spherical particles were probably produced by condensation of lignin and its re-precipitation on the fiber surface. This process is usually accompanied by dissolution and migration of lignin within the cell wall layers, which has been proven to be important for improving cellulose digestibility.[15] Enzymatic hydrolysis of the pretreated substrates indicated that PMo_{12} and PW_{12} could obtain a high cellulose digestibility with a conversion of approximately 80 % within 24 h hydrolysis by heat-reduced pretreatment (Figure 3). $PMo_{11}V$ obtained somewhat lower conversion, and the solar-induced pretreatment achieved a lesser degree of digestibility. However, compared with untreated

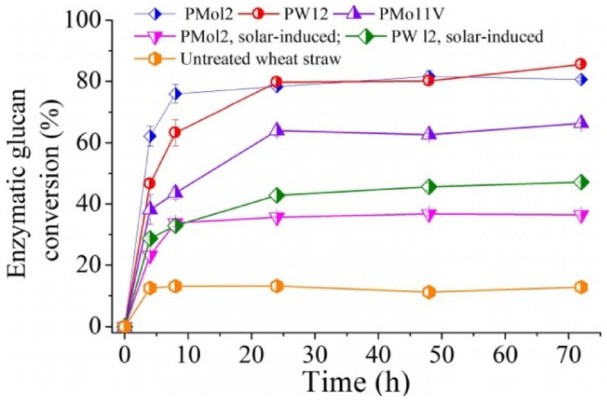

Figure 3. Enzymatic hydrolysis of POM-pretreated wheat straw for production of glucose. The heat-induced pretreatment was performed at 95 °C with 0.25 M POM for 45 min with the addition of 0.1 M phosphoric acid based on the results of the parameter optimization shown in Table S1 (Supporting Information). The solar-induced pretreatment was performed in a 100 mL conical glass flask in clear sunlight using 0.25 M POM and the addition of 0.1 M phosphoric acid for 12 h.

wheat straw, the enzymatic glucan conversion was greatly improved.

It should be noted that enzymatic digestibility of the pretreated substrates was just one of the most important response variables to be considered for the POM pretreatments. Other aspects such as polysaccharides (cellulose and hemicellulose) dissolution, degree of delignification, and reduction degree of POM should also be considered to achieve the highest biomass conversion efficiency with a maximum energy or exergy recovery. We performed a series of experiments to investigate effects of various factors on pretreatment process (Table S1, Supporting), and determined that the temperature and POM concentrations were the most important factors (these data will be published in a subsequent study). Significant dissolution of polysaccharide and condensation of lignin were observed at temperatures higher than 140 °C, and the highest enzymatic digestibility of cellulose was obtained at 100–120 °C; the optimal temperature to obtain the highest reduction of PMo_{12} was 140 °C. It should be noted that POMs are usually sensitive to pH values and acidic strength, because POMs can function as both electron and proton carriers, and the addition of electrons decreases the acidity of the POM, which is also accompanied by protonation.[11] However, in our experiments, we found that the addition of an external mineral acid such as H_3PO_4 showed no significant influence on the pretreatment. This was probably because the high concentration of POMs (0.25 M) used in the experiments could provide high enough acidity, and the addition of H_3PO_4 at a relatively low concentration (< 0.1 M) thus yielded no significant change on the acidity of the system. With consideration of the effects of several factors on various response variables, the optimal "charging" condition was 95 °C with 0.25 M POM concentration, which was close to that used for discharging of the reduced POM in the fuel cell. Under this condition, less polysaccharide dissolution (≈30% of cellulose and 50% of hemicellulose) was achieved than the process performed at 100–120 °C, but with similar enzymatic glucan conversion (about 80%); however, the reduction degree of POM decreased to approximately 50%, compared to about 80% at 140 °C.

The re-oxidation of reduced POM in a liquid flow fuel cell (or redox flow cell) also generates electricity. Due to its suitable redox properties and high photochemical activity, POM has been employed for intensifying electricity generation and electrochemical processes.[16–18] However, increasing the cathode reaction rate is important for improving the cell power output. The typical cathode used for proton exchange membrane fuel cells (PEMFCs) is made of carbon paper with gas diffusion layers and covered with Pt catalyst. However, this cathode does not yet obtain a high power density (< 1 mW cm^{-2}) for direct biomass fuel cells.[11,12] The discharging efficiency could be improved greatly by using liquid catalysts or oxidants, and POM also has been found to be good electron mediator for the cathode to transfer an electron to oxygen.[12,13] In the present work, we compared several commonly used liquid oxidants for discharging reduced PMo_{12} (Table 1). $KMnO_4$ achieved a high power density due to its high redox potential, especially if the cathodic reaction took place with the addition of external H^+ (standard electrode potential $E^0 = 1.70$ V, under acidic conditions). $FeCl_3$ showed much higher power output (3.84 mW cm^{-2}) than $CuCl_2$ (0.63 mW cm^{-2}), which was even higher than that obtained by $KMnO_4$ without the addition of external H^+ (2.09 mW cm^{-2}). Therefore, Fe^{3+} was screened as a promising liquid oxidant for discharging. More importantly, Fe^{3+} is much cheaper than POMs, and the Fe^{3+} can be easily regenerated by oxidation of the Fe^{2+} by air at low temperatures, which can fulfill using air as the final electron acceptor for electricity generation.

It was determined that the oxidation of $FeSO_4$ by O_2 in an aqueous system has a rate constant of 1.49 L mol^{-1} min^{-1} with an activation of 35 kJ mol^{-1}.[19] The rate of oxidation of Fe^{2+} to Fe^{3+} is also dependent upon the nature of the anion present, and increases as the complexing affinity of the anion to ferric iron increases. Under acidic conditions, the rate was determined to decrease in the order of hydroxide > pyrophosphate > phosphate > chloride > sulfate > perchlorate.[20] However, for the aerobic re-oxidation of the POMs, temperatures of 150–200 °C and an O_2 pressure of 0.6–0.8 MPa are usually used.[10] We compared three commonly used ferric salts, namely $FeCl_3$, $Fe_2(SO_4)_3$, and $Fe(NO_3)_3$, as cathode electron mediator at an Fe^{3+} concentration of 0.8 M for discharging. As shown in Figure 4A, $Fe(NO_3)_3$ obtained the highest power density (7.29 mW cm^{-1-2} at 80 °C) with 610 mV open circuit voltage (OCV) followed by $FeCl_3$ ($P_{max} = 7.04$ mW cm^{-1-2} and 496 mV OCV), and $Fe_2(SO_4)_3$ showed the lowest power output ($P_{max} = 4.86$ mW cm^{-1-2} and 456 mV OCV). However, it should be noted that if $Fe(NO_3)_3$ is used, NO_3^- is oxidative and also takes part in the cathodic reaction with the formation of some derivative products. Therefore, it is not a suitable electron mediator for discharging, and $FeCl_3$ is the most promising candidate.

For Fe^{3+} as an electron mediator in the cathode, the anode half-cell reaction [Eq. (2)], cathode half-cell reaction

Table 1. Comparison of different liquid oxidants used in the cathode vessel for discharging of reduced PMo_{12} at 70 °C.

Cathode oxidant	Cathodic reaction	$E^{0[a]}$ [V]	P_{max} [mW cm^{-2}]	$I_{2\Omega}$ [mA] after 8 h
0.8 M $FeCl_3$	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	3.84	16.5
0.8 M $CuCl_2$	$Cu^{2+} + Cl^- + e^- \rightarrow CuCl$	0.56	0.63	12.4
0.16 M $KMnO_4$	$MnO_4^- + 3e^- + 2H_2O \rightarrow MnO_2 + 4OH^-$	0.59	2.09	4.5
0.16 M $KMnO_4$ (1.28 M H^+)	$MnO_4^- + 3e^- + 4H^+ \rightarrow MnO_2 + 2H_2O$	1.70	14.52	2.4
0.4 M H_2O_2 (0.8 M H^+)	$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O$	1.78	0.99	8.1

[a] Standard electrode potentials.

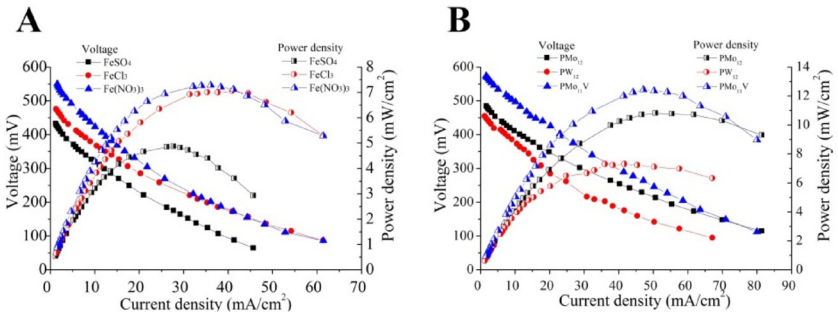

Figure 4. Effects of some ferric salts on discharging of reduced PMo_{12} at 80 °C (A); comparison of discharging of several reduced Keggin-type POMs for electricity generation at 90 °C (B).

[Eq. (3)], and total cell reaction [Eq. (4)] can be simply expressed as follows:

$$Mo^{5+} \rightarrow Mo^{6+} + e^-,\ E^{\ominus} = 0.50\,V \quad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+},\ E^{\ominus} = 0.77\,V \quad (3)$$

$$Mo^{5+} + Fe^{3+} \rightarrow Mo^{6+} + Fe^{2+},\ E^{\ominus}_{mf} = 0.77 - 0.50 = 0.27\,V \quad (4)$$

The Nernst equation [Eq. (5)] of the total cell potential (E_{TC}) is:

$$E_{tc} = E^{\ominus}_{mf} - \frac{RT}{F}\ln\frac{[Fe^{2+}]\,[Mo^{6+}]}{[Fe^{3+}][Mo^{5+}]} \quad (5)$$

As shown in Equation (5), the cell potential is influenced by reaction temperature and the $[Fe^{3+}]/[Fe^{2+}]$ and $[Mo^{6+}]/[Mo^{5+}]$ ratios. Increasing temperature, Mo^{5+} concentration in anode solution, and Fe^{3+} concentration in the cathode solution are beneficial to enhancing the cell potential. For example, the standard cell potential $E^{\ominus}_{mf}$ is 0.27 V; however, if the discharging was performed at 90 °C with $[Fe^{3+}]/[Fe^{2+}] = 100$ and $[Mo^{6+}]/[Mo^{5+}] = 0.01$, the cell potential could be increased to 0.56 V. After investigating the effects of various operating parameters such as temperature, flow rate, Fe^{3+} concentration, external addition of H^+, and cell structural factors such as active electrode area and type of PEM (the data will be published in subsequent study), the highest output power density for discharging the reduced PMo_{12} could be as high as 10.8 $mW\,cm^{-2}$ with a Faraday efficiency of 97.4 %. The electricity generation by re-oxidation of different reduced POMs was further compared as shown in Figure 4B. $PMo_{11}V$ achieved the highest P_{max} (12.4 $mW\,cm^{-2}$), followed by PMo_{12} (10.80 $mW\,cm^{-2}$), whereas PW_{12} obtained the lowest P_{max} (7.30 $mW\,cm^{-2}$). However, as observed for the pretreatment process, $PMo_{11}V$ showed the poorest performance for enhancing the cellulose digestibility, and PMo_{12} and PW_{12} showed better performances. However, PW_{12} is less stable than PMo_{12} as observed for the pretreatment process, and thus PMo_{12} is the most promising POM to mediate the co-production of sugars and electricity from lignocellulosic biomass. The microbial fuel cell (MFC) is another fuel cell technology that can directly utilize lignin or lignin derivative phenols for electricity generation. However, the output power density of phenol-fueled MFCs is usually lower than 0.002 $mW\,cm^{-2}$,[12] and the power density obtained in the present work was 5000–6000 times higher; this is also approximately 10 times higher than that of the recently reported direct biomass fuel cell with an air cathode covered by Pt catalyst.[11,12]

The integrated process proposed in the present work can achieve a coproduction of fermentable sugars and electricity under mild conditions. In the ideal scenario, cellulose and hemicellulose are converted to sugars whereas the lignin is converted to electricity. Theoretically, from 100 g of wheat straw used in this work, 38.6 g glucose, 25.7 g xylose, and 21.1 g lignin could be obtained. If the lignin is completely oxidized to CO_2 and water, there would be approximately 3.6 mol of electrons transferring to the oxidant, which corresponds to 350 000 Coulombs of electric charge. In this work, the sugar yields were 21.8 g glucose and 5.4 g xylose per 100 g wheat straw with a transfer of 48 300 Coulombs of electric charges. The loss of sugars was mainly due to the dissolution and degradation of polysaccharides during POM pretreatment. For example, PMo_{12} pretreatment solubilized 28 % of the cellulose and 52.1 % of the xylan in the raw wheat straw. These solubilized polysaccharides would be difficult to recover for ethanol production. However, this hydrolysate may be also oxidized by POMs, because POMs can function as an electron-transfer/oxygen-transfer catalyst for oxidation of cellulose and hemicellulose to form degradation products such as formic acid, CO, and even CO_2 depending on reaction conditions.[21] Under the pretreatment conditions, POM oxidation of lignin mainly involves the oxidation of side chains, degradation of some inter-unit linkages, partial degradation of the benzene structure to form benzoquinone, and removal of the aliphatic and phenolic hydroxyl groups.[10,12,22] However, further oxidation of the degradation products by POM becomes more difficult. Therefore, to achieve high lignin-to-electricity generation, most of the C–C bonds must be oxidized by POMs, but this is not easy to achieve under mild conditions. Nevertheless, it should be noted that the phenolic compounds produced during POM pretreatments are usually valuable chemicals. The phenol deriv-

atives such as benzoic acid, *p*-hydroxy benzaldehyde, vanillin, acetovanillone, vanillic acid, veratraldehyde, veratric acid, syringaldehyde, acetosyringone, and 2,6-dimethoxy-*p*-benzoquinone have been identified in the solution as degradation products.[23] The profits of this integrated process would be more attractive if these valuable by-products can be economically recovered from the pretreatment liquid. It also should be noted that POMs are relatively expensive, and they must be recovered as much as possible from the pretreated slurry. A possible process to recover the POMs is displacement washing with volatile solvent, which can be easily recovered by evaporation. However, more studies on parameter optimization, kinetics, cell design, electrode development, process design, and optimization as well as energy efficiency analysis should be performed in the future to further improve the efficiency.

Moreover, this work also provides a novel idea for combination of the direct biomass fuel cell and redox flow cell to achieve a flexible switch of the system between electricity generation from biomass and energy storage (Figure 5). If

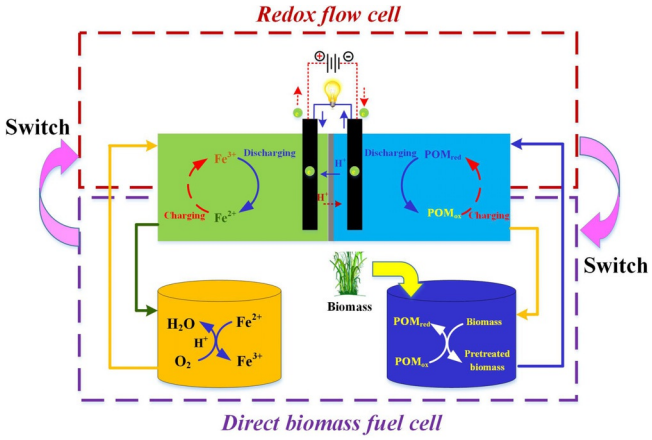

Figure 5. Conceptual combination of the POM/Fe^{3+} mediated redox flow cell and direct biomass fuel cell.

used as a direct biomass fuel cell, the system works following the principle shown in Figure 1B, in which electrons are transferred from biomass (lignin) to the POM, then to Fe^{3+}, and finally reach the oxygen. Upon switching to a redox flow cell, Fe^{2+}/Fe^{3+} and POM_{red}/POM_{ox} are used as redox couples to achieve charging and discharging for energy storage. In the charging process, Fe^{2+} is oxidized to Fe^{3+} in the positive chamber, and POM_{ox} is reduced to POM_{red} in the negative chamber. In the discharging process, the reverse reactions take place. Actually, POMs have been used as redox couples for redox flow batteries to achieve good stationary storage of energy. POMs are promising energy storage materials because they are capable of undergoing multi-electron reactions and are stable over a wide range of pH values and temperatures.[24,25] However, the properties and efficiency of this POM–iron battery have to be further investigated.

In conclusion, POMs are promising mediators to integrate biomass pretreatment and increase cellulose digestibility for the efficient conversion of a biomass component (particularly lignin) to electricity at low temperatures. In this integrated process, the POM was reduced mainly by the oxidation of lignin accompanied by dissolution of a considerable amount of hemicellulose, thus simultaneously improving cellulose accessibility for subsequent enzymatic hydrolysis. The pretreatment can be considered as a "charging" process. The reduced POM could be well re-oxidized in a liquid flow cell with electricity generation. Fe^{3+} ($FeCl_3$) was screened as an effective and promising liquid catalyst (mediator) to transfer electrons to air, as the final electron acceptor. This re-oxidation process is a "discharging" process with regeneration of the oxidizing POM. The highest power densities of 10.8 and 12.4 $mW\,cm^{-2}$ were obtained for discharging of reduced PMo_{12} and $PMo_{11}V$, respectively. This power density was 5000–6000 times higher than that of the phenol-fuel MFC, and 10 times higher than that of the recently reported direct biomass fuel cell with an air cathode covered by Pt catalyst. This system also can be combined with a POM–iron mediated redox flow battery to achieve a flexible switch between biomass pretreatment coupled with electricity generation (BPCEG) and energy storage. The finding of this work thus can provide a new method for biomass conversion.

Experimental Section

The experimental details are outlined in the Supporting Information.

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