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ARTICLE

Electro-catalytic oxidation of hemicelluloses at Au electrode

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The recently reported electro-catalytic reaction mechanism for oxidation of cellulose, is proposed to work also for the electro-oxidation of other polysaccharides (e.g. hemicelluloses). In this report, the electrochemical reactivity of some hemicelluloses (xylan, arabinoxylan, glucomannan, xyloglucan, and glucuronoxylan) in 1.3 M NaOH solution is described. The electrochemical property of each of the studied hemicelluloses at a Au electrode surface was characterized by cyclic voltammetry. Xylan, xyloglucan and glucuronoxylan were found to be electrochemically active. Electrochemical property of xylan was further studied by electrochemical impedance spectroscopy. The electrochemical reaction products of xylan, made by extensive electrolysis of the xylan solution by cyclic voltammetry, were characterized by FTIR spectroscopy, ^{13}C-NMR spectroscopy, SEM and TEM. The structural studies suggest that the oxidized xylan is a functional material where some of the OH-groups have been oxidized to carboxyl groups making that part of the oxidation product soluble in water under ambient conditions (23°C, pH 7). The other part remains insoluble in water and contains Au nano-particles. This work indicates that also other polysaccharides than cellulose can electrochemically be oxidized.

Introduction

Utilization of cellulosic biomass as an alternative material resource is expected to play an important role in building a sustainable society.[1,2] Especially the demand for production of new materials, as alternatives to petrochemical products, from the main components of the biomass resources has increased because they are environmentally-friendly and renewable materials on Earth.[2,3] The cellulosic biomass consist of three major components, i.e. cellulose, hemicelluloses and lignin. Because cellulose and hemicelluloses are composed of monosaccharide units such as glucose and xylan, they can be alternative renewable raw material for production of various valuable products including chemicals, functional materials (e.g. functional polymers and films) and fuels (e.g. hydrogen and ethanol).[1,4] Many different technologies have been developed to convert these polysaccharides, especially cellulose, into useful products.[5] Cellulose is a linear homopolymer of glucose units coupled with β-1,4-glycosidic linkages.[6] In general, glucose is a preferred material and more accessible as carbon source than xylose and other pentoses for the biochemical reactions in the biological system on Earth.[7]

Once glucose is obtained from cellulose by its degradation, several kind of products can be made from it by applying commonly used chemical and biochemical technologies. In fact, most of the valuable products such as biodegradable plastics, fuels (e.g. hydrogen and ethanol), organic acids (e.g. lactic acid), solvents (e.g. acetone) and other chemicals have been produced from cellulose.[2] However, despite being a major component in the cellulosic biomass, the utilization of hemicelluloses has so far been limited. Although some useful products (e.g. furfural) have been made from hemicelluloses, the number of applications of hemicelluloses is much smaller than those of cellulose. One of the barriers for utilization of hemicelluloses is that their monomeric units cannot be used in the same way as glucose in many chemical and biochemical applications, particularly in fermentation using microorganisms.[7,8] In the conventional process in converting cellulose and hemicelluloses to functional products e.g. by enzymatic processes several specific enzymes are required depending on the target molecule. The, in this work proposed, electro-catalytic oxidation process is a more general process in converting electrochemically active polysaccharides to useful products.

The electrochemical reactivity of some hemicelluloses at a Au electrode surface in 1.3 M NaOH solution is studied in this paper. Recently, direct electrochemical oxidation of cellulose using Au electrode has been demonstrated,[9,10] and its reaction mechanism has also been proposed.[10] This unique approach can result in a new technology for energy and material conversion from polysaccharides, because it can convert the water insoluble crystalline cellulose into water soluble oxidized cellulose on an electrode surface without any of the currently used conventional technologies such as saccharification and fermentation. The proposed reaction mechanism can be expected to be valid also for electro-catalytic conversion of other polysaccharides (e.g. hemicelluloses). Once it is confirmed that the electro-catalytic oxidation works for hemicelluloses, it would offer a new research field, electrochemistry of hemicelluloses, which has not so far been explored and would open novel routes for an alternative production of functional materials from the hemicelluloses. Unlike cellulose, hemicelluloses have various types of chemical structures having different branches and chemical groups on the macromolecule. This gives even new possibilities for production of several types of functional bio-polymers. Characterization of the basic electrochemical properties of hemicelluloses as presented in this work is important not only to develop a new reaction pathway for conversion of new functional materials but also to gain a general knowledge of the electro-catalytic reaction of the polysaccharides originating from the cellulosic biomass.

Materials and methods

Materials. Xylan (from birch wood) was obtained from Sigma-Aldrich. Arabinoxylan and xyloglucan were purchased from Megazyme. Glucomannan and glucuronoxylan were obtained from the Laboratory of Wood and Paper Chemistry at Åbo Akademi University. All other chemicals were of analytical reagent grade. Distilled, deionised water was used to prepare all solutions. 1-4 % (w/v) hemicellulose in 1.3 M NaOH solution was prepared and used as the stock solution in all electrochemical measurements.

Cyclic voltammetry (CV). All electrochemical measurements were performed by using a three-electrode electrochemical cell at room temperature (23°C±1°C). The working electrode (WE) was a Au disk (geometric area = 0.07 cm^2) and the counter electrode (CE) was a Pt wire. The reference electrode (RE) was a Ag/AgCl/KCl (3 M). All potentials were measured against this reference electrode. Electrochemical measurements were made by using an Autolab PGSTAT20 potentiostat/galvanostat using the General Purpose Electrochemical System (GPES). Prior to electrochemical measurements, the Au working electrode was cleaned by a physical procedure (polished with 0.3 µm alumina, rinsed with water and cleaned ultrasonically). If necessary, the physically polished electrode was additionally cleaned by a chemical way (immersed into a mixture of H_2SO_4 and H_2O_2 (3:1, v/v), rinsed with water and cleaned ultrasonically) and by an electrochemical treatment: applying potential cycling from -0.1 V to 1.2 V at 100 mVs^{-1} in 0.5 M H_2SO_4 until the CV became stable, rinsed with water and then cleaned ultrasonically. The electrolyte solution was initially purged with N_2 for 30 min and the experiments (CV and EIS) were performed under a N_2 atmosphere.

Electrochemical Impedance Spectroscopy (EIS). The impedance spectra were recorded with the amplitude of 10 mV in a frequency range of 100 kHz-10 mHz by using an Autolab PGSTAT20 Frequency Response Analyzer (FRA).

Sample preparation for structural analysis. In the structural analysis of the electro-oxidized xylan, the sample was dissolved in 1.3 M NaOH to make a 1% solution of xylan and the solution was then electrolyzed with 7000 potential scans between -0.4 and +0.4 V with the scan rate of 50 mV/s at a Au plate electrode (geometric area = 18 cm^2). After the electrolysis, the sample solution was neutralized with an ion-exchange resin (Dowex 50WX8 in hydrogen form) and then centrifuged (10000 rpm for 10 min) to collect the supernatant as the target sample fraction containing the electro-oxidized xylan. During the electrolysis 31 % of the starting material (xylan) was converted to the water soluble form. The water insoluble fraction was also collected at the same time. The water soluble fraction was then freeze-dried to obtain solid dry samples for the FTIR and NMR spectroscopic analyses. The sample preparation process is described in Scheme S1.[10]

Fourier transform infrared spectroscopy (FTIR). The FTIR-ATR spectra were recorded using a Harrick's VideoMVPTM single reflection diamond ATR accessory (incidence angle: 45°) having a horizontal and circular sampling area (diameter: 500 µm) and a built-in pressure applicator. The prepared dry samples were tightly pressed against the diamond crystal during the measurement. The VideoMVPTM ATR accessory was attached to the Bruker IFS 66S spectrometer equipped with a DTGS detector. Totally 32 interferograms were co-added for each spectrum. The spectra were recorded in the wavenumber range 4000-400 cm^{-1} with a resolution of 4 cm^{-1}.

Nuclear magnetic resonance spectroscopy (NMR). In the solid state ^{13}C-NMR measurement, the NMR spectra were recorded with Bruker Avance 400 MHz spectrometer equipped with 4 mm CP MAS probe; operating frequencies 399.75 MHz (^{1}H) and 100.52 MHz (^{13}C). The spectra were recorded under the following conditions: spinning rate 7 kHz and contact time of 3 ms.

Scanning electron microscopy (SEM). Xylan samples were mounted on carbon tape stages for taking the images. All SEM images of the samples were recorded by the Leo Gemini 1530 scanning electron microscope having a thermoNORAN X-ray detector.

Transmission electron microscopy (TEM). The water insoluble part of the electrolyzed xylan was suspended in H_2O, cast onto a Cu grid, and dried. The TEM images of the sample were recorded by using a JEM-1400 Plus instrument.

Inductively coupled plasma mass spectrometry (ICP-MS). The water insoluble part of the electrolyzed xylan was dissolved in a mixture of HCl and HNO_3 (3:1, v/v) in a microwave oven (Anton Paar, Multiwave 3000) and diluted with deionized water prior to the ICP-MS analysis (PerkinElmer, Elan 6100 DRC Plus). A commercial standard IMS-103 from Ultra Scientific (RI, USA) was used for calibration in the quantitative analysis.

Results and discussion

Cyclic voltammetry (CV):

Fig. 1 shows cyclic voltammograms (CVs), j-E curves, between -0.4 V and +0.4 V with the scan rate of 10 mV/s, of 1 % (w/v) hemicellulose in 1.3 M NaOH solution recorded at a Au electrode. In the CV of the 1.3 M NaOH solution as the background, two current peaks are observed: at -0.1 V and +0.27 V (*vs*. Ag/AgCl). The small peak at -0.1 V indicates

adsorption of the OH$^-$ ions on the Au electrode surface and the peak at +0.27 V suggests formation of Au oxide.[10]
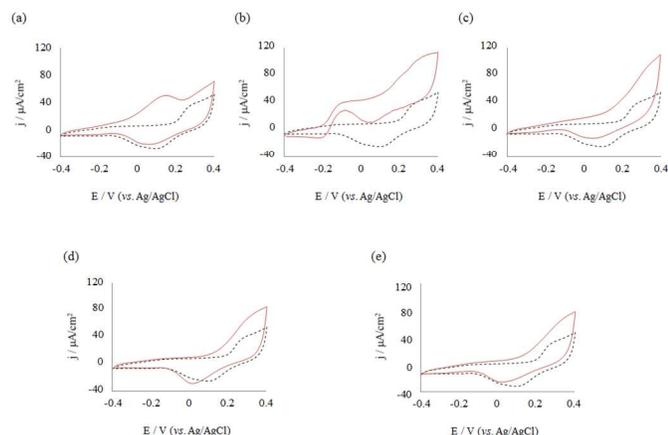
Figure 1. Cyclic voltammograms of 1 % (w/v) hemicelluloses at Au electrode in 1.3 M NaOH. (a) xylan, (b) xyloglucan, (c) glucuronoxylan, (d) arabinoxylan, (e) glucomannan. Black dash line: background. Scan rate: 10 mVs^{-1}.

The reduction peak at ca. 0.1 V in the reverse scan indicate reduction of the formed Au oxide.[10] In the solution of xylan, xyloglucan and glucuronoxylan, the current intensity at -0.1 V increased (Fig. 1 (a)-(c)) but in presence of arabinoxylan and glucomannan the wave at -0.1 V is rather suppressed (Fig. 1 (d) and (e)). In the solution of xylan, xyloglucan and glucuronoxylan an oxidation peak is observed between -0.1 V and +0.27 V (Fig. 1 (a)-(c)), while in the solution of arabinoxylan and glucomannan, no such peak was observed (Fig. 1 (d) and (e)). In the electro-oxidation of cellulose at a Au electrode in sodium hydroxide, the cellulose molecule starts to be oxidized after adsorption of OH$^-$ on the electrode surface and formation of OH-Au site at -0.1 V.[10] It can be proposed that the same process would take place also in the case of these electroactive hemicelluloses. In the case of xylan, the major oxidation peak is observed at 0.15 V. In case of xyloglucan strong increase in current is observed at -0.1 V and the oxidation peak is observed at ca. 0.19 V. The form of the CV of xyloglucan may also be influenced by the high viscosity of the solution. In the case of glucuronoxylan, the corresponding oxidation peak is observed at 0.22 V. These results indicate that these hemicellulose molecules are electrochemically oxidized at the Au electrode, whereas arabinoxylan and glucomannan do not show any noticeable oxidation current. It can, hence, be concluded from the observed results that the electrochemical reactivity of the hemicelluloses depends on their chemical structures, especially the chemical groups or branches attached to the main polymer chain (Fig. S1). The electro-inactivity of arabinoxylan may be due to the bulky side groups preventing the proper orientation of the molecule at the electrode surface which is the prerequisite for the electron transfer between the adsorbed molecule and the electrode surface. In the case of glucomannan the adsorption peak is very weak and no oxidation current is observed in Fig. 1 (e). Among the electro-active hemicellulose molecules xylan is slightly easier to be oxidized than the other studied hemicelluloses. In general, xylan has a linear polymer backbone composed of pentose units (xylose).[11] Compared with the electrochemical property of cellulose having a linear hexose-polymer of glucose, the oxidation peak potential of xylan (0.15 V vs. Ag/AgCl) is higher than the corresponding oxidation potential of cellulose

(0.05 V vs. Ag/AgCl).[10] This indicates that it is more difficult to oxidize hemicelluloses than cellulose in the electro-catalytic system using a Au electrode. Because xylan has the lowest oxidation potential of the studied hemicelluloses and shows simpler j-V curve in the CV, it was selected for more detailed characterization studies.

Fig. 2 shows CVs of xylan solution in different concentrations in 1.3 M NaOH recorded between -0.4 and 0.4 V at a Au electrode with the scan rate of 10 mVs^{-1}.
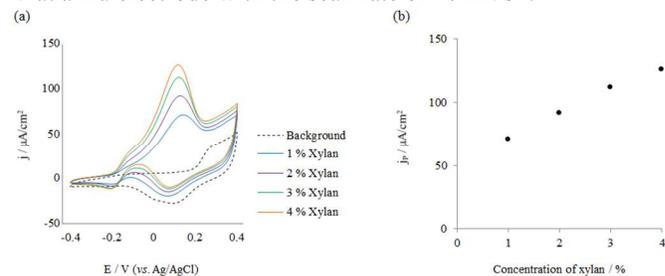
Figure 2. CVs of xylan in different concentrations. Scan rate: 10 mVs^{-1}.

In the presence of xylan, an oxidation peak can be observed in the potential range, where the background is rather flat. The current of the peak increases linearly with the concentration of xylan (inset in Fig. 2). This result indicates that the detected current signal is derived from oxidation of xylan at the Au electrode surface and can be used in quantitative determination of xylan. The positive peak at ca. -0.05 V on the reverse scan is due to desorption of the oxidation products of xylan simultaneously revealing the previously blocked electrode surface and allowing new xylan molecules to be oxidized at this potential. Similar oxidation current was found and discussed previously in the case of oxidation of cellulose.[10]

Fig. 3 (a) shows CVs of a 1 % (w/v) solution of xylan in 1.3 M NaOH at different scan rates.
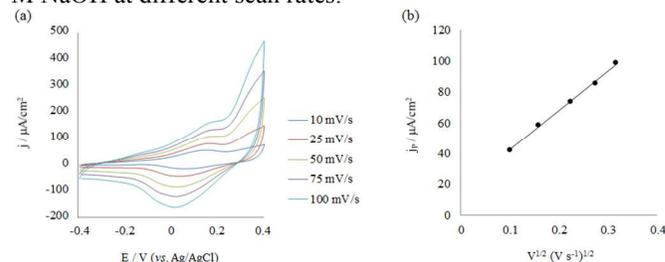
Figure 3. (a) CVs of 1 % (w/v) xylan in 1.3 M NaOH measured at different scan rates (10, 25, 50, 75, 100 mVs^{-1}). (b) j_P vs. $v^{1/2}$.

The intensity of the oxidation peak increases with increasing scan rate. The dependence of the peak current density on square root of the scan rate ($v^{1/2}$) is shown in Fig. 3 (b) (The plots are background corrected.). The current density (j_P) at the oxidation peak of xylan is linearly proportional to $v^{1/2}$ indicating a diffusion-controlled electrode process. Moreover, because there is no corresponding reduction peak in the CVs of xylan, it also indicates that the overall electro-oxidation process of xylan is an irreversible process.

Electrochemical Impedance Spectroscopy (EIS):

Fig. 4 shows the impedance spectra of 1 % and 4 % (w/v) xylan in 1.3 M NaOH at the Au electrode at different dc-potentials. The impedance spectra of the background electrolyte (1.3 M NaOH) without xylan are also shown in Fig. 4. At the potential -0.3 V (Fig. 4 (a)) the Nyquist diagrams show a

slightly smaller semicircle in presence of xylan than in the background electrolyte.
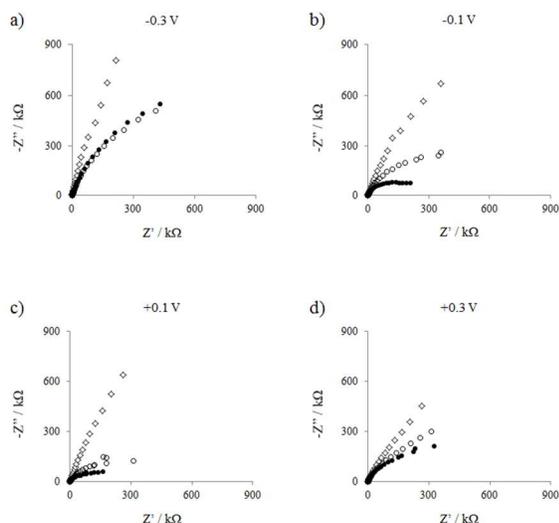
Figure 4. Impedance spectra of xylan in 1.3 M NaOH at different potentials. (a) -0.3 V, (b) -0.1 V, (c) 0.1 V, (d) 0.3 V. WE: Au, RE: Ag/AgCl, CE: Pt. Frequency: 10 mHz to 100 kHz. Background: ◊, with 1 % xylan: ○, with 4 % xylan: ●.

However, the impedance plot is very similar for 1 % and 4 % xylan, indicating that xylan mainly takes part in adsorption processes at -0.3 V (Fig. 4 (a)). On the contrary, at the potentials -0.1 V (Fig. 4 (b)) and +0.1 V (Fig. 4 (c)) the diameter of the semicircle in the electrolyte with xylan is significantly smaller than in the background and decreases with increasing concentration of xylan. This indicates that a charge-transfer process takes place between xylan and the electrode surface at -0.1 and +0.1 V, which is in the potential range of the oxidation peak in CV (Fig. 2). At 0.3 V (Fig. 4 (d)), the Nyquist plots with and without xylan again show similar semicircles indicating the formation of Au oxide taking place in both cases. The impedance data suggest that xylan shows the highest electrochemical activity around +0.1 V, which is in agreement with the results obtained by CV.

Fourier transform infrared spectroscopy (FTIR):

  The spectra (a) and (b) in Fig. 6 are from the original (before dissolution) and regenerated xylan (the sample has gone through the preparation procedure without any electrolysis, see scheme S1), respectively.
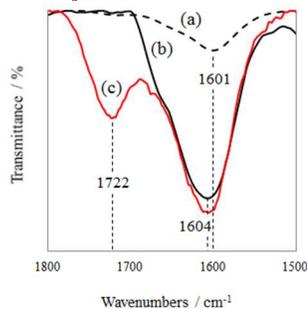
Figure 6. FTIR spectra of xylan samples before and after the electrolysis: (a) xylan before the dissolution, (b) regenerated xylan and (c) water soluble electrolyzed xylan. WE: Au, RE: Ag/AgCl, CE: Pt. The electrolysis process was performed with 7000 scans in the potential range from -0.4 V to 0.4 V with the scan rate of 50 mVs^{-1}.

Increase of the band at around 1604 cm^{-1} may be due to the increase of the amount of detectable carbonyl groups caused by the dissolution process of crystalline xylan. The spectrum (c) is obtained from the water soluble electrolysis product. Appearance of a new band at 1722 cm^{-1} in the spectrum (c) indicates that changes resulting in new C=O groups[12] have taken place in the xylan structure.

Nuclear magnetic resonance spectroscopy (NMR):

The original xylan sample and the electrochemically oxidized xylan were analyzed by CP MAS ^{13}C solid state NMR spectroscopy. The obtained spectra are shown in Fig. S2. The intensity of the signal at 167 ppm (corresponding to the carboxylic acid functionalities) is clearly increased as a result of the electrochemical oxidation. The new groups have been created through ring opening and/or oxidation of the ends of the polymer chains. More detailed study is under way in our laboratory.

Scanning electron microscopy (SEM):

  Fig. 7 shows SEM images of xylan samples before and after the electrolysis procedure.
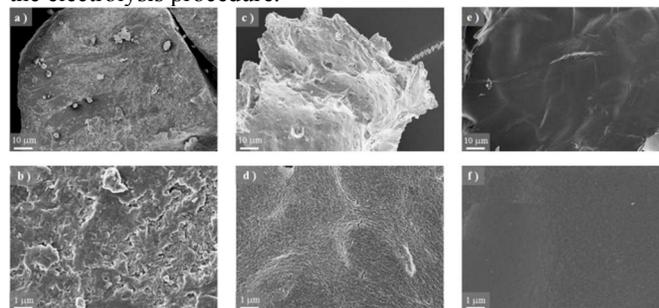
Figure 7. SEM images of xylan before and after the electrolysis. (a) and (b) original xylan before dissolution, different magnifications. (c) and (d) regenerated xylan, same magnifications as in (a) and (b). (e) and (f) the water soluble fraction after the electrolysis, same magnifications as in (a) and (b).

As can be seen in the comparison between the original (Fig. 7 (a) and (b)) and regenerated xylan (Fig. 7 (c) and (d)), the sample preparation process (i.e. dissolution) has also a slight smoothening effect on the morphology of the xylan sample. The surface morphology of xylan has, however, become significantly smoother after the electro-oxidation (Fig. 7 (e) and (f)). Similar phenomenon was also observed in the electro-oxidation of cellulose at a Au electrode.[10] These results indicate that the water soluble xylan derivative where some hydroxyl groups are oxidized to carboxyl groups has a smooth structural morphology.

Transmission electron microscopy (TEM):

  Fig. 8 shows TEM images of water insoluble xylan sample after the electrolysis. The white and gray areas indicate the surface of the grid stage. The black area in the center shows a fragment of the xylan sample. The black dots in the fragment are metal particles. In the quantitative elemental analysis using ICP-MS, Au was detected in the water insoluble xylan after the electrolysis (Table S1). This indicates that the black dots are Au nanoparticles (approx. 4-20 nm diameter) and that the water insoluble hybrid material composed of xylan and Au nanoparticles is also obtained by the electro-catalytic oxidation of xylan, the same way as in cellulose with Au nanoparticles.[10] The Au nano-particles are formed during the potential cycling when on the forward scan some gold at the electrode surface is oxidized and then reduced back to gold on the reverse scan.
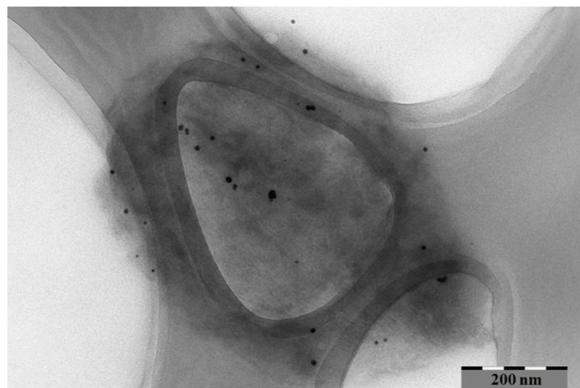
Figure 8. TEM images of water insoluble xylan after the electrolysis.

Reaction scheme:
Based on the results presented in this study a similar reaction scheme may be proposed for oxidation of hemicellulose as was proposed for oxidation of cellulose in ref. 10.

Conclusions

Basic information about the electrochemical reactivity of some hemicelluloses at a Au electrode was obtained. It was demonstrated that the hemicelluloses: xylan, xyloglucan and glucuronoxylan, can electrochemically be oxidized at the Au electrode surface in alkaline solution. The oxidation peak potentials of these electro-active hemicelluloses are more positive than the peak potential of cellulose. It was demonstrated that the electrochemical oxidation of xylan results in oxidation of some hydroxyl groups to carboxyl groups in the xylan molecule. The electro-oxidized xylan is a functional material and easily soluble in water. The water insoluble fraction of the electro-oxidized xylan contains Au nano-particles formed during the electrolysis procedure. It is proposed that the electro-catalytic reaction at the Au substrate can be applied for oxidative functionalization of some hemicelluloses. Dissociation of the OH groups in the hemicellulose molecule, polyole, may also have a positive effect on the electro-oxidation of hemicellulose at Au electrode.[13]

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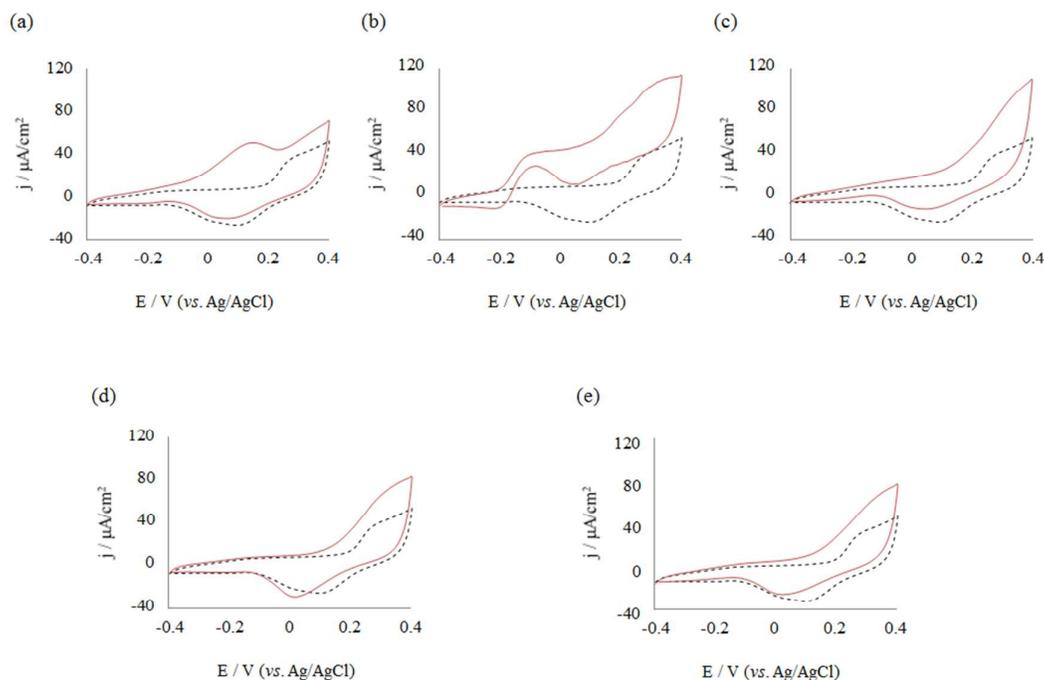
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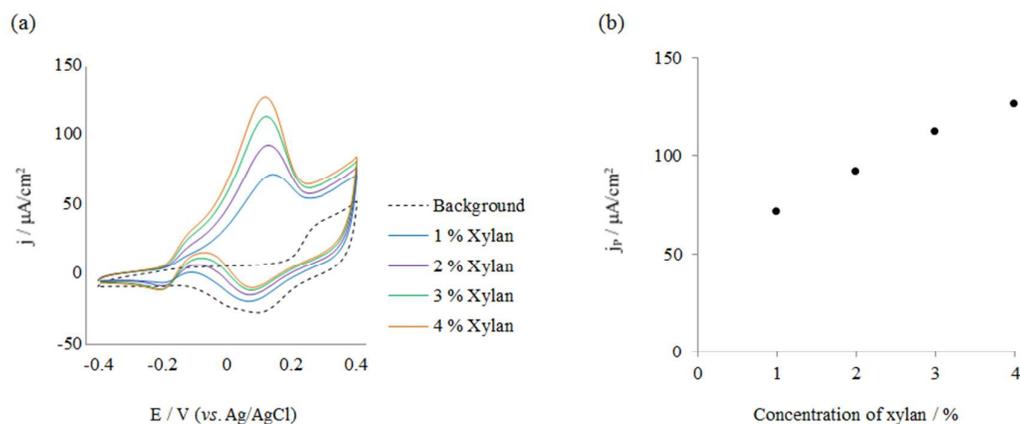
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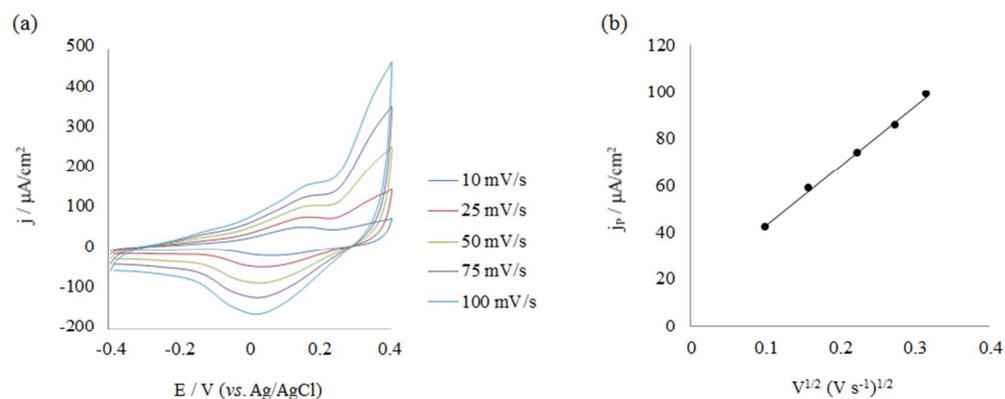
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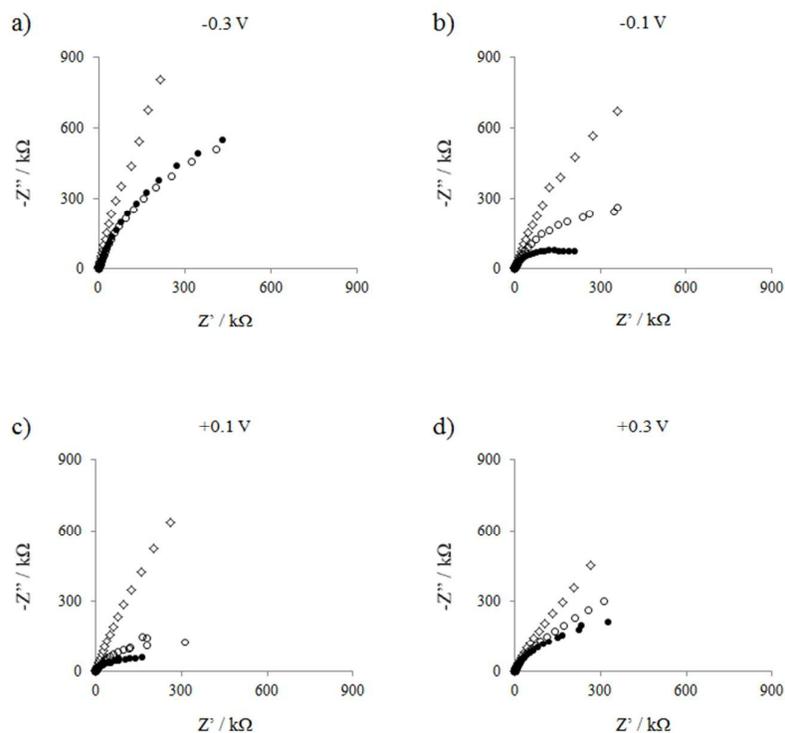
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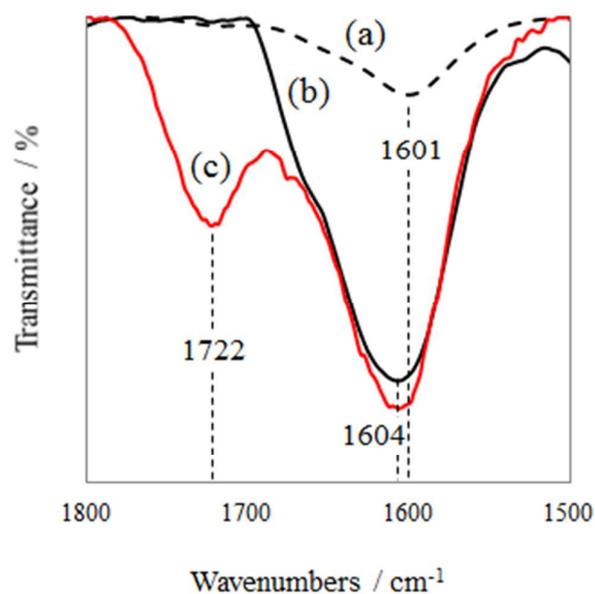
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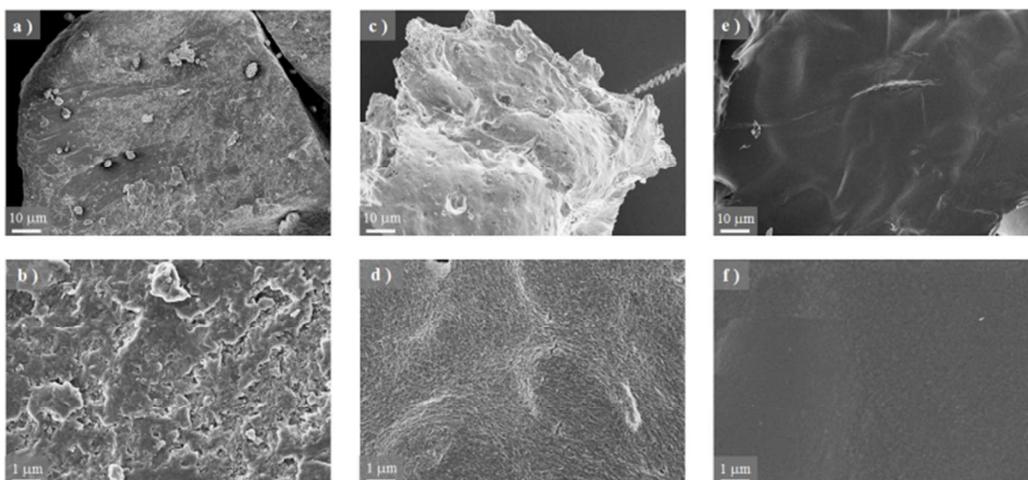
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