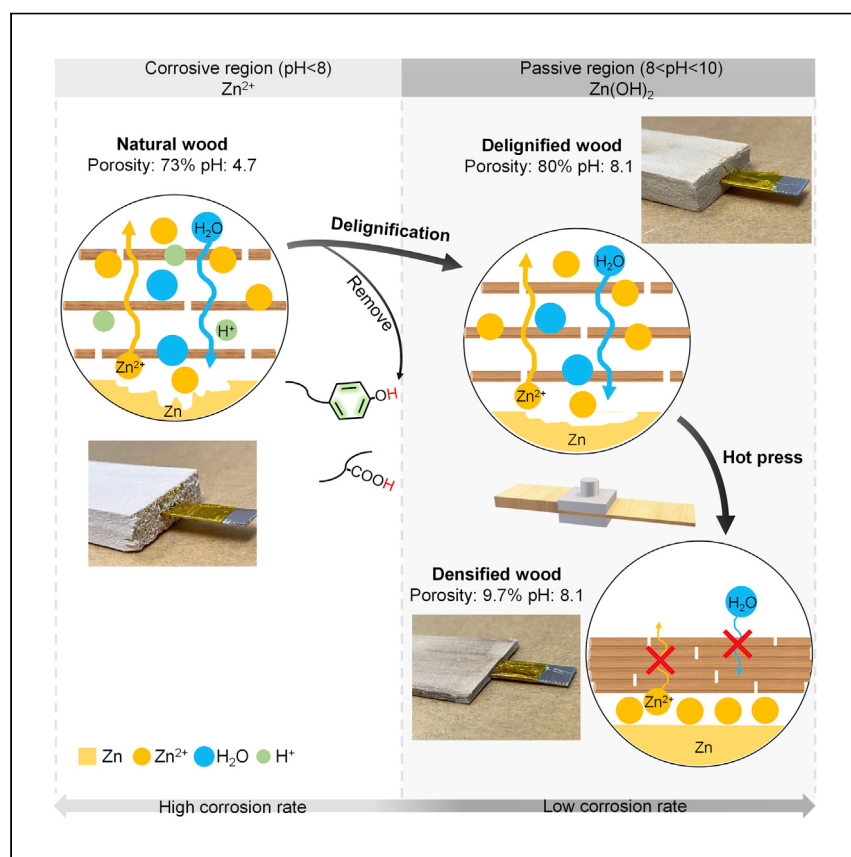


Article

A low-corrosivity structural timber



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Highlights

Delignified and densified wood is
a minimally corrosive material
toward metals

Delignification reduces the acidity
of wood

Densification reduces the ionic
transport in wood

Anisotropic structure makes wood
densification effective in reducing
ion transport

Delignified and densified wood is a mechanically strong and minimally corrosive material. Yu et al. report that delignification raises the pH value of wood and minimizes further acidic products even at elevated temperatures. Densification is effective in reducing ion transport. These two factors effectively suppress corrosion of galvanized steel, despite being in a hydrophilic material.

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Article

A low-corrosivity structural timber

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SUMMARY

While densified wood emerges as a promising candidate to replace metals in structural applications, joining densified wood is critical to extend its size and shape for practical applications. Here, we investigate the roles of chemical composition and material microstructure in determining corrosion rates by studying the behavior of galvanized low-carbon steel embedded in three wood materials: natural basswood, delignified wood, and densified wood. Delignification selectively reduces acidic precursors, hemicelluloses and lignin, in wood and increases its pH value, which is also more stable at elevated temperatures. Though delignification causes densified wood to be more hydrophilic, the highly dense structure significantly reduces ion diffusion in wood. Both delignification and densification lead to exceptionally low corrosion rates for metal embedded within densified wood. This work sheds light on new approaches to corrosion resistance that can be applied to a broad range of uses for engineered wood.

INTRODUCTION

Engineered wood is an emerging structural material.^{1–4} It is light, strong, and sustainable. Treatment of natural wood with an alkaline solution followed by compression yields densified wood with a mechanical strength that rivals those of structural metals.⁵ Chemical process partially removes lignin and hemicelluloses from wood so that compression can enable the complete collapse of the porous structure in the wood and the formation of strong hydrogen bonding between the remaining cellulose fibers. Engineered wood opens new application potentials in a range of technology areas, from vehicles and buildings to thermal insulation and light management.^{6–10} Wide adoption of engineered wood will have a profound impact on sustainability, since most structural materials (e.g., metals, polymer fiber composites, and concrete) are produced with a large carbon footprint. For use of engineering wood in integrated structures, integration with metals is often needed to form extended structures or complex three-dimensional (3D) shapes. To maintain the high mechanical strength of the integrated structure, the metal/wood joint strength needs to remain unchanged over the service lifetime of the structure.^{11–13} However, metal corrosion in wood structures is a well-known phenomenon.^{14–17} In the timber industry, moisture and acetic acid are the biggest threats to metal being used with timber.¹⁸ Densified delignified wood (densified wood) is known to be more hydrophilic after the chemical treatment, which may accelerate galvanic corrosion of the metal.^{5,14} However, no studies have been done on the corrosion behavior of metals embedded in densified wood.

In this report, we investigate the corrosion of galvanized low-carbon steel (GCS) in engineered wood. Specifically, we compare the corrosion rates in natural wood

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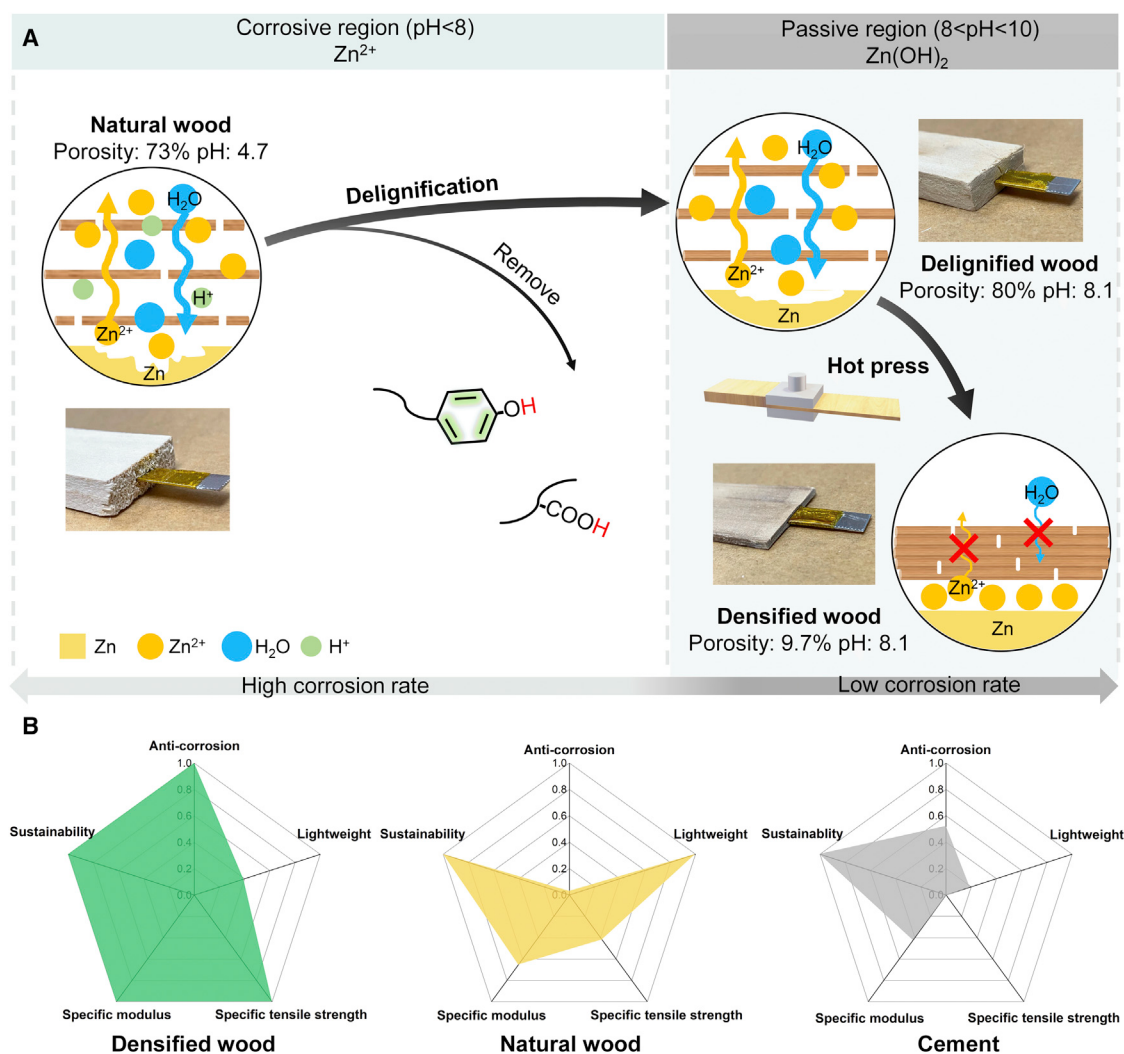


Figure 1. Completely derived from natural wood, densified wood with a weak alkaline environment and low-porosity structure can be used as a low-corrosivity structural timber

(A) Schematics of the metal corrosion embedded in natural wood, delignified wood, and densified wood, respectively.
(B) Performance comparison of densified wood, natural wood, and cement. All woods mentioned here are basswood.

(basswood), delignified wood after a chemical treatment, and densified wood after a delignification and compression process (Figure 1A). In studying these three materials, we decouple the roles of chemical composition and material microstructure in determining corrosion rates. Chemical treatment changes the pH value of wood from slightly acidic to slightly basic as measured by the wood extract (pH of ~ 4.7 increases to ~ 8.1 after treatment). Densification is expected to reduce the transport rates of water and dissolved metal ions.

We have found that both reducing acidity and densification are beneficial in reducing the corrosion rates of GCS embedded in wood. Our findings are important for future engineered-wood designs. Their low corrosivity, coupled with high strength, light weight, and sustainable production, makes engineered wood highly desirable over typical structural materials like concrete (Figure 1B).^{17,19–22} The densified wood also overcomes the corrosive nature suffered by basswood itself. Further, our work points to new directions of a low-corrosivity wood-structure design.

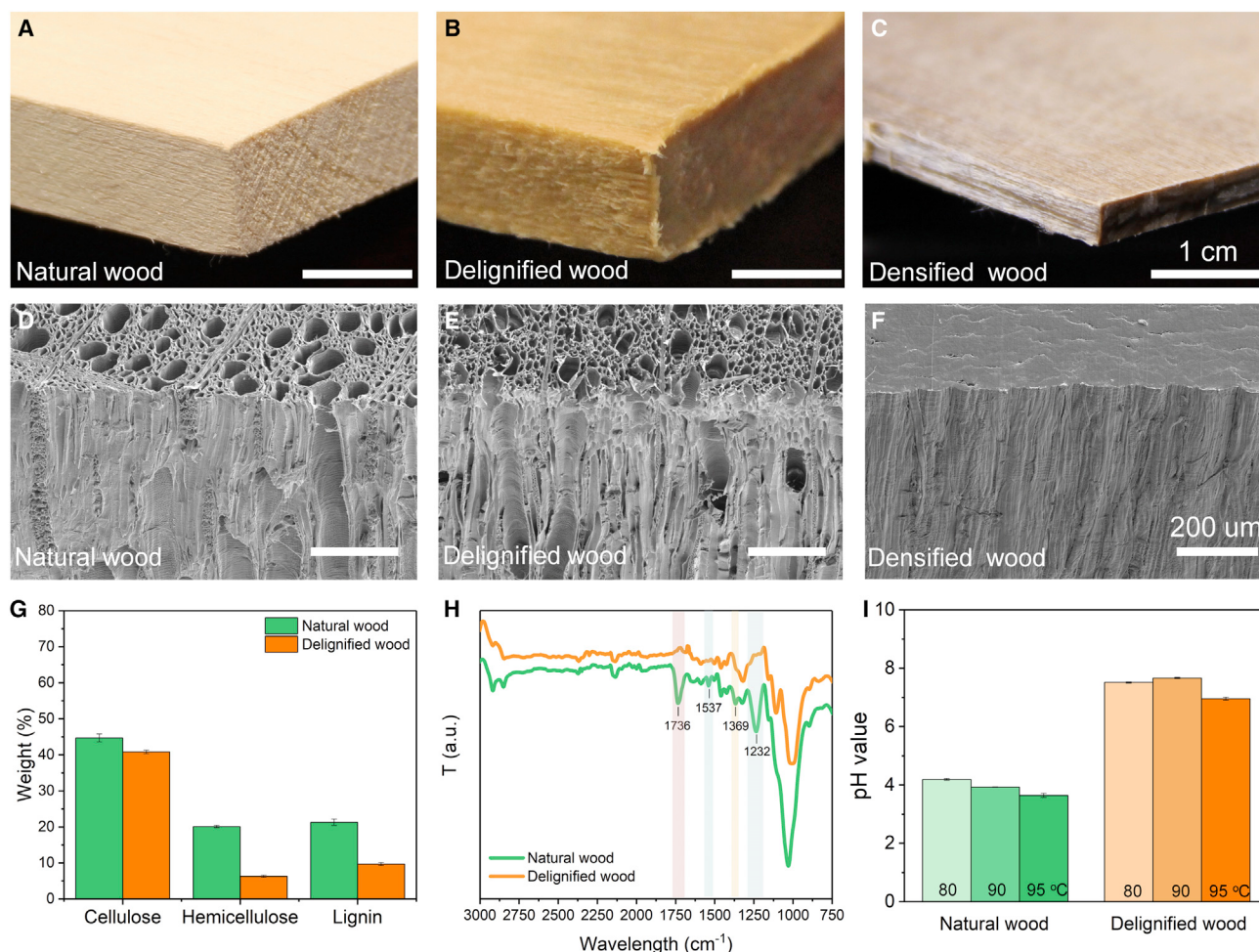


Figure 2. Characterizations of natural wood, delignified wood, and densified wood

(A–F) Digital photograph (A–C) and SEM images (D–F) of natural wood, delignified wood, and densified wood. The scale bars in (A–C) are 1 cm and in (D–F) are 200 μm .

(G) Composition analysis (normalized by natural wood).

(H and I) IR spectra (H) and pH evaluations (I) of natural wood and delignified wood at 80°C, 90°C, and 95°C (left to right). The error bars describe the ranges of three repeated data points.

Common strategies on corrosion prevention focus on the use of preservatives and thermal treatment to reduce hygroscopicity of the structure since minimizing water is expected to reduce ion transport and interfacial reaction rates.^{16,17,23} In contrast, our work shows that elimination of acidity and porosity are highly effective methods for reducing corrosion.

RESULTS AND DISCUSSION

Fabrication of densified wood

We employ a two-step approach for the fabrication of a weakly alkaline, dense, and mechanically strong material by a direct chemical treatment of natural wood followed by hot pressing, which is referred to as “densified wood” (Figures 1A and 2A–2C; see Experimental procedures). The default time of chemical treatment (delignification) is 8 h unless otherwise noted. The combined delignification-compression process reduces the thickness of natural wood to about 20% of its original value and forms a dense, low-porosity structure (Figures 2D–2F). Natural wood has a high

porosity and many intrinsic tubular channels (lumina, 20–80 μm in diameter), which are essential to the fast transmission of nutrients and moisture in the wood (Figure 2D).²⁴ The presence of lignin and hemicelluloses within the cellulosic fiber wall imparts strength and rigidity to trees.²⁵ A direct hot pressing of natural wood without chemical treatment leaves many gaps in between collapsed cell walls (Figure S1). In contrast, delignification reduces the amount of lignin and hemicellulose in the cellulosic fiber wall leading to a softer structure while not changing the thickness (no collapse of pores; Figure 2E). When hot pressed at 100°C perpendicular to the growth direction of the delignified wood, the tubular channels and the porous wood walls completely collapse, resulting in both the thickness and porosity of the wood being reduced to about 20% (Figures 2C, 2F, and S1). Quantitative values are provided in Table S1 based on density measurement rather than N_2 -adsorption measurements, which did not yield appreciable adsorption (Figure S2).

While chemical treatment can partially remove lignin/hemicellulose from the wood cell walls, there is much less cellulose loss because of the different stabilities of these three components in the $\text{NaOH}/\text{Na}_2\text{SO}_3$ solution (Figure 2G). The method of wood composition analysis is shown in the Experimental procedures. Meanwhile, most acidic functional groups in the rest of lignin/hemicellulose are removed, as shown by Fourier-transform infrared (FTIR) analysis (Figures 2H and S3). Peaks at 1,537, 1,369, and 1,232 cm^{-1} are associated with lignin. The 1,736 cm^{-1} peak represents carbonyl groups in lignin and acetyl groups in hemicelluloses, with the latter being the source of acetic acid.^{26–28} These peaks disappear after the chemical treatment. Therefore, the delignified wood becomes a weak alkaline material with better thermal stability impeding acidification even at elevated temperatures (Figures 2I and S3). Dispersion of natural wood particles in water yields a pH of 4.70. Heating to 80°C and holding for 96 h results in a pH of 4.19. In contrast, the pH of delignified-wood samples only decreases from 8.10 to 7.25 even after 96 h at 95°C. Ideally, the pH of delignified wood should be ~ 7 instead of ~ 8.1 . The actual source of the additional alkalinity is mostly likely due to residues of hydroxides and/or sulfite in wood; however, the amount of these residues is very limited as there is no obvious pH increase under evaluation at elevated temperatures over four days (Figure S4).

Influence of chemical delignification on corrosion behavior

We evaluated the influence of chemical delignification on the corrosion behavior of GCS in a wood extract¹⁵ or directly embedded in the solid wood structure (Figure 3; see Experimental procedures). The surface of the GCS is covered with a zinc coating. In the wood extract, the rate of metal corrosion is purely determined by the chemical properties of wood. Compared with the natural-wood extract, GCS in the delignified-wood extract exhibits a more positive corrosion potential and an order-of-magnitude decrease in corrosion current (Figure 3B). For the corrosion curve, the left branch corresponds to oxygen reduction and/or hydrogen evolution (cathodic reaction), and the right branch represents metal oxidation (anodic reaction).^{29,30} A shift of pH changes the corrosion potential to a more positive value. Based on the Pourbaix diagram, zinc corrosion products in natural-wood extract are soluble (Zn^{2+} , pH = 4.7) but precipitate as $\text{Zn}(\text{OH})_2$ at a pH of 8.1, the condition formed by delignified wood.³¹ X-ray photoelectron spectroscopy (XPS) indeed showed the presence of Zn–OH on the surface of corroded GCS in densified delignified wood (Figure S5), which confirmed the formation of $\text{Zn}(\text{OH})_2$. The zinc hydroxide passive layer possibly impedes the process of both cathodic and anodic reactions.^{30,32} The corrosion rate is determined by the charge-transfer process. Electrochemical impedance spectroscopy (EIS) results (Figure S6) indeed show that the values of charge-transfer resistance (R_{ct}) of two GCS electrodes in the

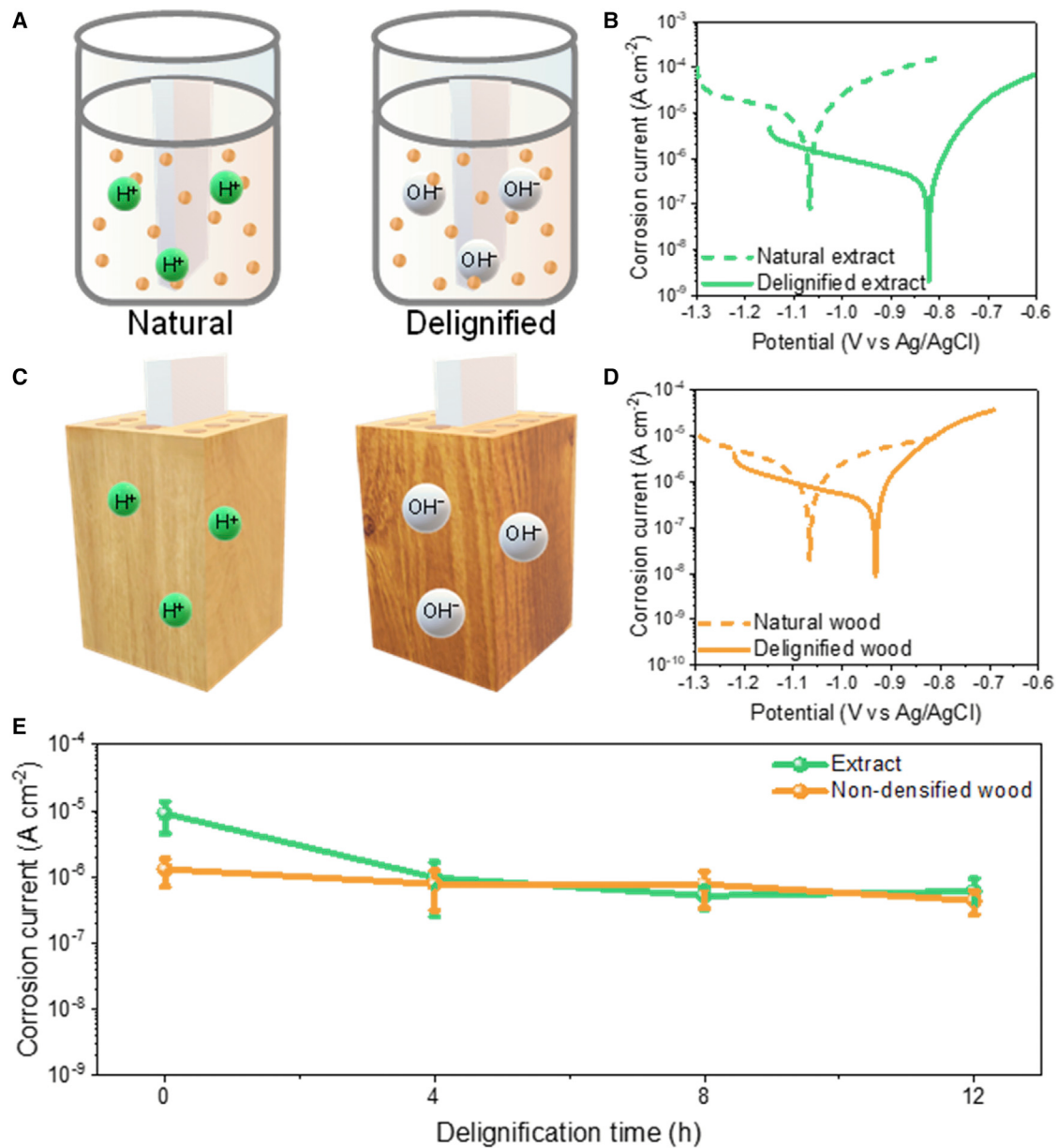


Figure 3. The chemical influence on corrosion rate

(A) Schematics of the GCS soaked in natural-wood extract and delignified-wood extract, respectively.

(B) Potentiodynamic polarization curves for GCS in natural-wood extract and delignified-wood extract, respectively, at scan rate 10 mV min⁻¹ and at 298 K.

(C) Schematics of the GCS embedded in natural wood and delignified wood.

(D) Potentiodynamic polarization curves for GCS in natural wood and delignified wood at a scan rate 10 mV min⁻¹ and at 298 K.

(E) A summary of corrosion rates of GCS in extract and non-densified wood with different delignification times. The error bars describe the ranges of three repeated data points.

delignified-wood extract are at least one order-of-magnitude larger than in the natural-wood extract.

We also evaluated the corrosion rates when GCS is embedded in the natural- and delignified-wood samples (Figure 3C). In this test, the wood structure with the embedded metal is soaked in a wood extract and serves as the working electrode.

Both natural wood and delignified wood have high porosities and many micro-level tubular channels. The porosity of natural wood is 73%. The porosities of delignified wood with different delignification times are 78.7% (4 h), 80% (8 h), and 81.3% (12 h) (Figure S3C). As a result, mass transport of water and ions is not expected to be impeded, and the corrosion rates should be largely determined by pH. Indeed, Figure 3D shows that delignified wood exhibited a more positive corrosion potential and a decrease in corrosion rate. Finally, we also investigated the effect of delignification time (from 4 to 12 h). The longer delignification time did not reduce corrosion rates further (Figure 3E). This observation is consistent with the similar chemical compositions in delignified-wood samples (Figure S3).

Structural factors influence on corrosion behavior

We next evaluate the structural influence (porosity of wood) on the corrosion behavior of GCS embedded in wood. In porous wood (Figure 4A), ions and water move freely as in bulk solution. When densified (Figure 4B), the structure of wood substrates is expected to reduce the free-water content and impede the diffusion of chemicals. As a result, the concentration of the zinc ion, $c(\text{Zn}^{2+})$, a corrosion product, is expected to be higher at the metal/wood interface (Figure 4B).³¹ Thermodynamically, the $c(\text{Zn}^{2+})$ at the zinc surface has a strong impact on the corrosion rate (i_c) and corrosion potential (E_c) (Figure S7). An increase of $c(\text{Zn}^{2+})$ will lead to a decrease in the corrosion rate and a positive shift in the corrosion potential. Kinetically, the transport of ions is slower when the wood is densified. EIS results (Figures S8 and S9) indeed show that the ionic resistance (R_{ionic}) of densified wood is one order-of-magnitude larger than the wood extract or the non-densified wood. It is worth mentioning that the ionic conductivity of wood is influenced by both delignification and densification. Delignification makes the wood more hydrophilic and promotes ion conduction. Densification for a given material always reduces ion conduction. These two factors combined led to the observed higher conductivity for densified delignified wood than that of the densified natural basswood. The lower rate of ionic transport impedes the anodic and cathodic reactions during metal corrosion leading to a lower corrosion rate. The lower corrosion rates after densification of either natural wood or those after different degrees of delignification are consistent with these explanations (Figures 4D and 4E). Furthermore, the long-term corrosion rates of GCS in natural wood and densified wood are evaluated by storing metal-wood samples under a relative humidity of 100% over 1 year (Figure S10; see Experimental procedures). The corrosion rate of GCS in natural wood is $0.86 \pm 0.27 \mu\text{A}/\text{cm}^2$. In contrast, the corrosion rate of GCS in densified wood is $0.22 \pm 0.02 \mu\text{A}/\text{cm}^2$. The long-term corrosion rates show the same trend as those observed in electrochemical tests. Densified wood exhibits a much lower corrosivity than natural wood.

We have observed the influence of both chemical and microstructure on the corrosion rate, i_{measured} . To quantitatively understand the corrosion rate (Figures 3 and 4; Table S1), we adopt a recently published quantitative model for metal corrosion in concrete to describe the effect of the porosity of the wood:³³

$$i_{\text{measured}} = i_{\text{max}} \times \frac{1}{2} \left(1 + \frac{P - P_{\text{crit}}}{\sqrt{k + (P - P_{\text{crit}})^2}} \right) \quad (\text{Equation 1})$$

where i_{max} represents the maximum corrosion rate of a metal in a completely open system (i.e., a solution or a highly porous structure) without any constraint of diffusion rates imposed by the substrate. p is the porosity of the substrate. P_{crit} is defined as the transition point between a condition of the system behaving as in a bulk

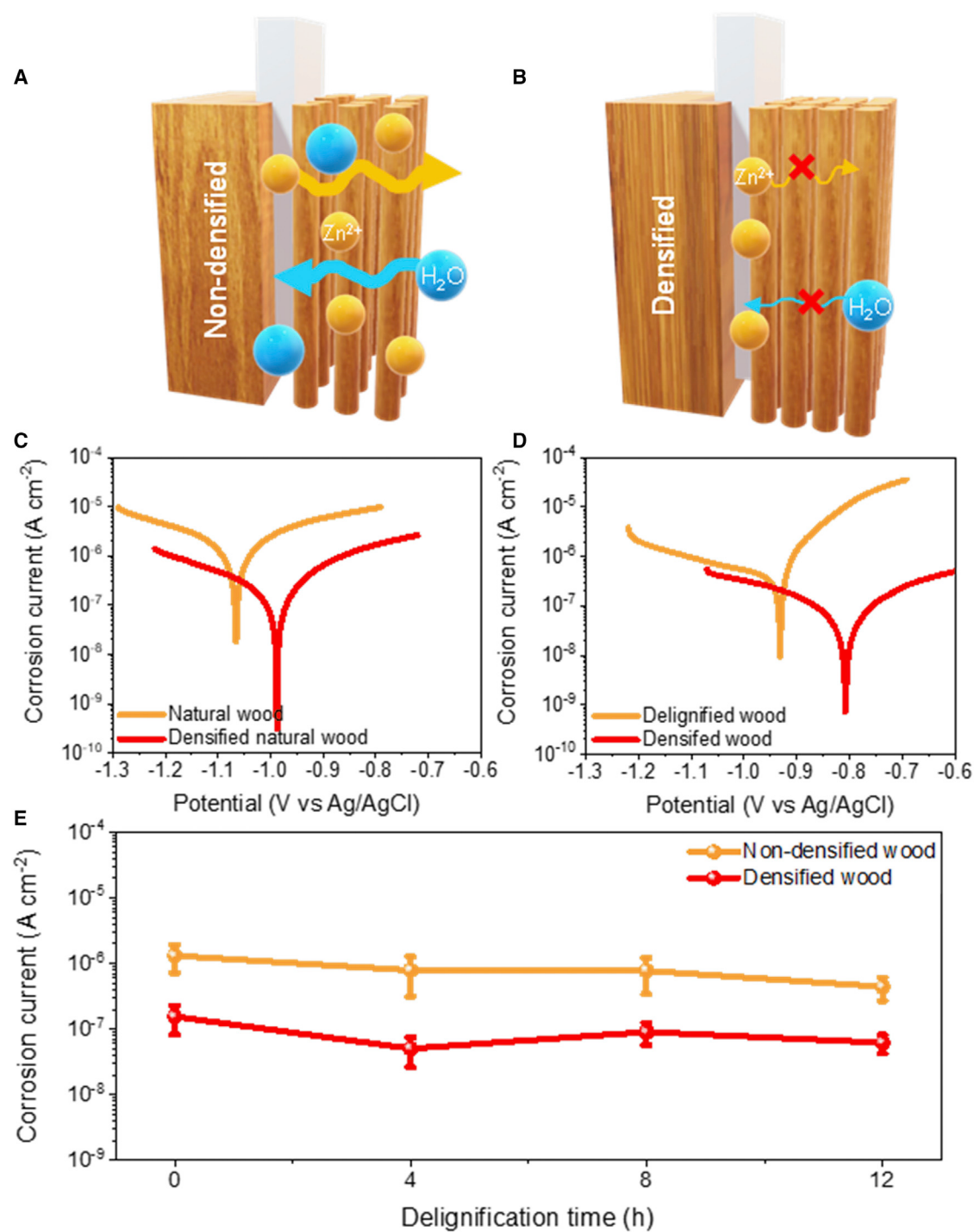


Figure 4. The structural influence on corrosion rate

(A and B) Schematics of the metal corrosion embedded in (A) high-porosity wood and (B) low-porosity wood.

(C) Potentiodynamic polarization curves for GCS embedded in natural wood and densified wood in corresponding extracts at a scan rate of 10 mV min^{-1} and at 298 K .

(D) Potentiodynamic polarization curves for GCS embedded in delignified wood and densified wood in corresponding extracts at a scan rate 10 mV min^{-1} and at 298 K .

(E) A summary of corrosion rates of GCS in non-densified wood and densified wood with different delignification times. The error bars describe the ranges of three repeated data points.

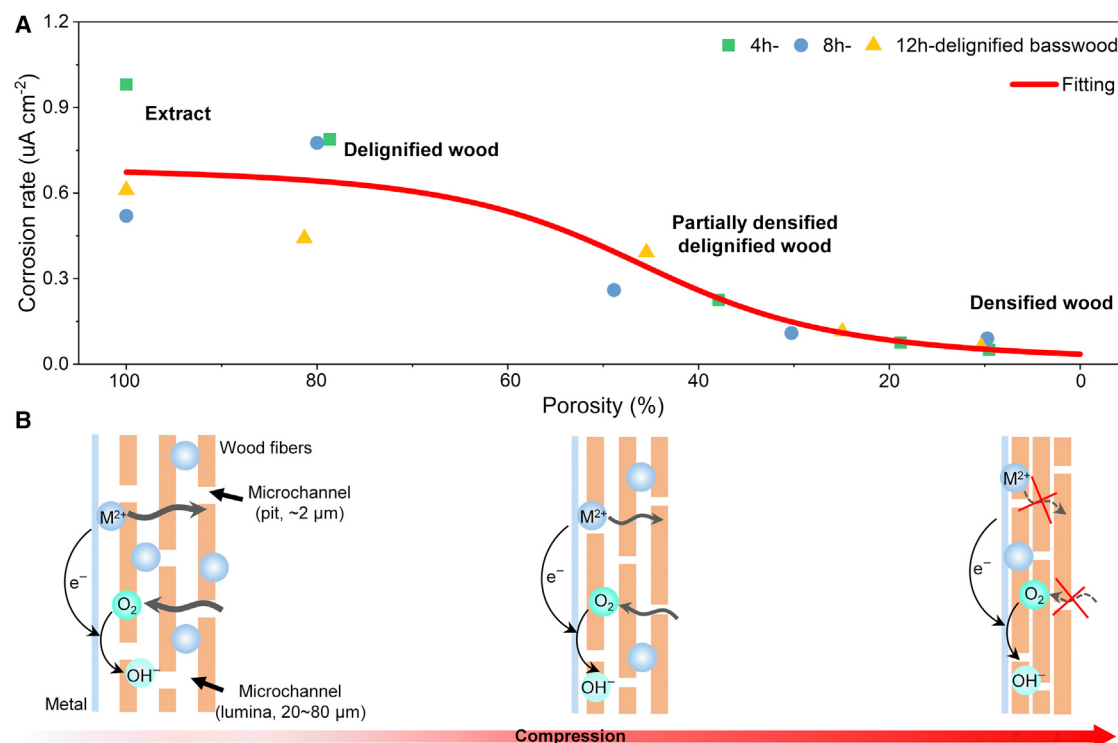


Figure 5. Mathematical model of corrosion rate of metal as a function of the porosity of substrate

(A) Relationship between the corrosion rate of embedded GCS and the porosity of densified-wood substrate. Dots represent the average experimental value for a given sample, while the solid line is the result of fitting per Equation 1 ($i_{max} = 0.7 \mu\text{A cm}^{-2}$, $P_{crit} = 0.46$, and $k = 0.05$).

(B) Schematic diagram exhibits the relationship between the corrosion rate of embedded metal and the porosity of wood-like substrates.

solution and one where the ion transport is controlled by the pore structure. The constant k describes the effect of total porosity on the probability of change of pore interconnectivity.³³

Fitting results based on this model unveil how the microstructure influences corrosion rates (Figure 5A). At high porosities, the system behaves as in a bulk solution. Reducing the porosity of substrate (wood) has no significant influence on ion/water diffusion and the corrosion rate of $0.7 \mu\text{A cm}^{-2}$, the fitting results of i_{max} , until p approaches P_{crit} (0.46). At this point, a small decrease in porosity causes a steep reduction in corrosion rate. The slope of this transition region between p of 0.46 to 0.2 depends on the k constant, which is a measure of the degree of pore interconnectivity. Here, the k value is equal to 0.05. We have found that data obtained from wood samples fabricated from different delignification times can all be fitted with this model, which is reasonable since all of the wood samples have similar physical structures.

It is informative to compare our results with those reported for metal in cement, which have a k value of ~ 0.001 and a P_{crit} of 0.185.³³ The values of k and P_{crit} depend on the microstructure (Figure 5B). Cement has an isotropic structure. Though the P_{crit} of cement is lower than wood, decreasing porosity near P_{crit} rapidly reduces ionic transport since the probability of pore interconnectivity decreases quickly (formation of dead ends or closed pores), which corresponds to a small k value. In contrast, wood has an anisotropic structure where the ionic transport is fastest along the wood-growth direction. Decreasing porosity near P_{crit} has a lesser effect on corrosion current since the pore interconnectivity is better maintained: a single

passage between two parallel channels will maintain connectivity. In addition, the hydrophilic pore walls themselves may also contribute to ion conduction. This is consistent with previous reports that dense but highly aligned and hydrophilic structure tubular channels still provide good ionic diffusivity.^{10,34} Hence, wood exhibits a large k value. On the other hand, the higher P_{crit} of densified wood means that the anisotropic structure experiences the onset of ion transport limitation sooner than the isotropic structure of cement. Compression is very effective in continuously reducing the size of tubular channels.

We have thus shown that densified wood is a mechanically strong and minimally corrosive material. Delignification raises the pH value of the wood and minimizes further production of acids even at elevated temperatures. Densification is very effective in reducing ion transport. These two factors effectively suppress corrosion of galvanized steel despite being in a hydrophilic material. This work demonstrates the potential use of densified wood in metal-wood integrated structures for sustainable, weight-sensitive structures. Our work has mainly evaluated the embedded corrosion of metal in fixed-thickness (porosity) timbers with saturated moisture levels. Further work is needed to consider other conditions, such as the effect of temperature, salt, and moisture levels.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for the resources are available from the lead contact, Ping Liu (piliu@eng.ucsd.edu).

Materials availability

The delignified wood and densified wood generated in this study are available from the [lead contact](#) upon reasonable request.

Data and code availability

The data that support the findings of this study are available from the [lead contact](#) upon reasonable request.

Materials and chemicals

All basswood samples were purchased from Midwest Products. Sodium hydroxide (>97%, Sigma-Aldrich) and sodium sulfite (>98%, Sigma-Aldrich) and deionized (DI) water were used for wood processing.

Preparation of delignified wood

First, natural-wood blocks (typical sample dimension: 8 × 3 × 0.375 inches) were immersed in a boiling aqueous solution of mixed 2.5 M NaOH and 0.4 M Na₂SO₃ for 4 to 12 h, followed by immersion for several times in boiling DI water to remove the chemicals. Next, the wood blocks were cut to a suitable size (3 × 1 × 0.375 inches) for the corrosion test. The first described dimension is the length along the direction of wood growth.

Wood-composition analysis

The lignin content was measured based on Technical Association of Pulp and Paper Industry Standard Method T 222-om-83. Specifically, 1.0000 g dry wood (m₀) was extracted with ethanol for 4 h to remove resin, fat, and wax. The extracted wood powder was then treated with cold H₂SO₄ (72%, 15 mL) for 2 h at 20°C. Then, the mixtures were transferred to a beaker, diluted to 3 wt % H₂SO₄ by adding 560 mL of DI water, and boiled for 4 h. Finally, they were filtered and washed with DI water.

The insoluble materials were dried and weighed (m_1). The lignin content is calculated as: $(m_1/m_0) \times 100\%$.

The cellulose content was measured by the following method. First, 1.0000 g dry wood (m_0) and 25 mL nitric acid-alcohol mixture (the volume ratio of concentrated nitric acid to ethanol is 1:4) was added into a 250 mL flask, then the mixture was refluxed for 1 h in a boiling-water bath. This operation was repeated several times until the fiber became completely white. Finally, the residue in the flask was transferred into a sand core funnel with a known weight of m_1 , washed with DI water to neutrality, dried in an oven at 105°C to a constant weight, and weighed (m_2). The cellulose content is calculated as: $(m_2 - m_1)/m_0 \times 100\%$.

Holocellulose refers to the cellulose and hemicellulose in the raw materials of plants. To determine the content of hemicellulose, we first measured the holocellulose content. 2.000 g dry wood (m_0) was extracted with a benzene/ethanol solution (the volume ratio of benzene to ethanol [95% in water] is 2:1) for 6 h and then air dried. The wood sample, 0.6 g of sodium chlorite, 0.5 mL of glacial acetic acid, and 65 mL of distilled water were added into a 250 mL Erlenmeyer flask, which was covered with a 25 mL small Erlenmeyer flask and heated in a water bath at 75°C for 1 h. Then, 0.6 g of sodium chlorite and 0.5 mL of glacial acetic acid was added into the Erlenmeyer flask and heated at 75°C for another 1 h. This operation was repeated several times until the fiber became completely white. Finally, the residue in the flask was transferred into a sand core funnel with a known weight of m_1 , washed with DI water to neutrality, dried in an oven at 105°C to a constant weight, and weighed (m_2). The holocellulose content is calculated as: $(m_2 - m_1)/m_0 \times 100\%$. The hemicellulose content is equal to the holocellulose content minus the cellulose content.

Preparation of wood extract

This method was reported by Zelinka et al.¹⁵ For the preparation of wood extract, sawdust was added to DI water at a weight ratio of 1:10. The mixtures were sealed in 120 mL glass vials and stored for 1 week at room temperature. After the extraction period, the sawdust was separated out, and the clear solution was employed in the experiment, referred to as wood extract.

Preparation of metal-wood couple

All wood samples were pre-soaked in boiling water for 1 h and cooled down to room temperature by washing with DI water. GCS sheets (1.25 × 0.25 × 0.026 inches) were ultrasonically cleaned with a soap solution, rinsed with DI water, further degreased by acetone, rinsed again with DI water, and then inserted into wood samples (1 × 0.375 inches) with pre-drilled holes (1 inch in depth). The pre-drilled holes (1 × 0.25 × 0.026 inches) were in turn created by driving a piece of GCS sheet into the wood. For densified wood, metal-wood couples were compressed under a pressure of about 5 MPa at 100°C for about 1 day to obtain the densified wood (3 × 1 × ~0.08 inches). As densified wood in the extract solution has swelling issues, we employed two plates to fix the thickness of densified wood during the corrosion evaluations. In Figure 5, we controlled the distance between the plates to let densified wood swell to “partially densified” states (0.1 and 0.12 inches thick, respectively) in the extract solution.

Electrochemical tests

Corrosion evaluations were carried out using a three-electrode cell set up controlled by a CHI660E potentiostat. The working electrode is a GCS sheet

(0.25 × 1.25 × 0.026 inches). For the metal in wood-extract experiments, a 0.5 inch² region of the sheet was immersed in the extract solution. For the metal in wood samples, they were pre-soaked in extract for 3 days. Pre-soaking the sample in the extract helps to ensure the interface between metal and wood is fully wet. We use the extract solution in order to minimize the change in the wood composition, which includes the leaching of ions if water is used. We also think that the extract solution is preferred over a neutral salt electrolyte, which might still change the solution composition at the wood/metal interface. Platinum wire and Ag/AgCl electrode (pre-soaked in potassium chloride solution) served as the counter and reference electrodes, respectively. Potentiodynamic polarization curves were obtained by scanning from a potential from -250 to +250 mV versus open-circuit potential (OCP) at a scan rate of 10 mV min⁻¹.

The EIS measurements were carried out using a two-electrode configuration controlled by a Biologic electrochemical system (VSP-300). Two GCS sheets were used as the electrodes (1 cm² in active area). The frequency range was 7 MHz to 0.1 Hz. For experiments performed in the extract solution, two electrodes were positioned 1 inch apart in parallel. For experiments performed in the wood samples, non-densified wood (1 × 0.25 × 0.25 inches) and densified wood (1 × 0.25 × ~0.05 inches) were pre-soaked in extract for 3 days. The wood sample was then sandwiched between two electrodes along the wood-growth direction. Meanwhile, two insulated plates were employed to fix the thickness of wood during the test. All experiments were conducted under ambient conditions at room temperature. For each condition, three repeated data points were obtained.

Long-term corrosion test

Clean GCS sheets (1 × 0.25 × 0.026 inches) were fully inserted into wood samples with pre-drilled holes. For natural wood, the metal-wood couples were dried at 60 °C in the vacuum oven for about 1 day. For densified wood, metal-wood couples were dried and compressed under a pressure of about 5 MPa at 100 °C for about 1 day. Then, metal-wood couples were stored in lab-made humidity boxes. The relative humidity in the box is 100%, balanced by DI-water (stored in one beaker inside the box). Every month during the long-term corrosion test, we opened the humidity box to refill DI water and then sealed it again. The corrosion rate of metal in wood was determined by the weight loss after removing corrosion products. The weight of fresh metal is designated as m₀. After 1 year of corrosion tests, we excavated the metal from the wood and carefully removed the corrosion products with a steel blade. After this process, the weight of metal is designated as m₁. The corrosion rate of metal in wood is calculated as (m₀ - m₁)/(area × time). For each condition, three samples were tested.

pH test

Sawdust was added to DI water at a weight ratio of 1:10. For room-temperature evaluation, the pH of the extract was measured after 1 week of storage. For elevated-temperature evaluation (80 °C, 90 °C, and 95 °C), the pH of the extract was measured after designated time: 0, 1, 2, and 4 days. During the extraction period, mixtures were sealed in 25 mL glass vials. All pH values were measured by a Multi-Parameter Smart Tester (LLC-AI3719 PC60-Z, Apera Instruments). Each condition contains three repeated data points.

Structural characterizations

A scanning electron microscope (SEM; Hitachi SU-70) was used to characterize the morphology of the wood samples. Infrared spectra were obtained on a ThermoScientific Nicolet 6,700 system.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.xcrp.2022.100921>.

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AUTHOR CONTRIBUTIONS

S.Y., P.L., and L.H. designed the experiments. S.Y. carried out corrosion evaluation and data analysis. Y.L. carried out the wood-composition analysis. S.Y., Y.L., and S.F. carried out material characterization. All authors contributed to the writing of the manuscript. C.C. and A.P.S. revised the manuscript. All authors commented on the final manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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REFERENCES

- Chen, C., Kuang, Y., Zhu, S., Burgert, I., Keplinger, T., Gong, A., Li, T., Berglund, L., Eichhorn, S.J., and Hu, L. (2020). Structure–property–function relationships of natural and engineered wood. *Nat. Rev. Mater.* 5, 642–666. <https://doi.org/10.1038/s41578-020-0195-z>.
- He, S., Chen, C., Li, T., Song, J., Zhao, X., Kuang, Y., Liu, Y., Pei, Y., Hitz, E., Kong, W., et al. (2020). An energy-efficient, wood-derived structural material enabled by pore structure engineering towards building efficiency. *Small Methods* 4, 1900747. <https://doi.org/10.1002/smt.201900747>.
- Hildebrandt, J., Hagemann, N., and Thrän, D. (2017). The contribution of wood-based construction materials for leveraging a low carbon building sector in Europe. *Sustain. Cities Soc.* 34, 405–418. <https://doi.org/10.1016/j.scs.2017.06.013>.
- Kitek Kuzman, M., Klarić, S., Pirc Barčič, A., Vlosky, R.P., Janakieska, M.M., and Grošelj, P. (2018). Architect perceptions of engineered wood products: an exploratory study of selected countries in Central and Southeast Europe. *Constr. Build. Mater.* 179, 360–370. <https://doi.org/10.1016/j.conbuildmat.2018.05.164>.
- Song, J., Chen, C., Zhu, S., Zhu, M., Dai, J., Ray, U., Li, Y., Kuang, Y., Li, Y., Quispe, N., et al. (2018). Processing bulk natural wood into a high-performance structural material. *Nature* 554, 224–228. <https://doi.org/10.1038/nature25476>.
- Li, T., Zhai, Y., He, S., Gan, W., Wei, Z., Heidarinejad, M., Dalgo, D., Mi, R., Zhao, X., Song, J., et al. (2019). A radiative cooling structural material. *Science* 364, 760–763. <https://doi.org/10.1126/science.aau9101>.
- Jiang, F., Li, T., Li, Y., Zhang, Y., Gong, A., Dai, J., Hitz, E., Luo, W., and Hu, L. (2018). Wood-based nanotechnologies toward sustainability. *Adv. Mater.* 30, 1703453. <https://doi.org/10.1002/adma.201703453>.
- Gan, W., Chen, C., Wang, Z., Song, J., Kuang, Y., He, S., Mi, R., Sunderland, P.B., and Hu, L. (2019). Dense, self-formed char layer enables a fire-retardant wood structural material. *Adv. Funct. Mater.* 29, 1807444. <https://doi.org/10.1002/adfm.201807444>.
- Zhu, M., Song, J., Li, T., Gong, A., Wang, Y., Dai, J., Yao, Y., Luo, W., Henderson, D., and Hu, L. (2016). Highly anisotropic, highly transparent wood composites. *Adv. Mater.* 28, 5181–5187. <https://doi.org/10.1002/adma.201600427>.
- Chen, G., Li, T., Chen, C., Wang, C., Liu, Y., Kong, W., Liu, D., Jiang, B., He, S., Kuang, Y., and Hu, L. (2019). A highly conductive cationic wood membrane. *Adv. Funct. Mater.* 29, 1902772. <https://doi.org/10.1002/adfm.201902772>.
- Nguyen, M.N., Leicester, R.H., Wang, C.H., and Foliente, G.C. (2013). Corrosion effects in the structural design of metal fasteners for timber construction. *Struct. Infrastruct. Eng.* 9, 275–284. <https://doi.org/10.1080/15732479.2010.546416>.
- Zelinka, S.L., and Rammer, D.R. (2012). Modeling the effect of nail corrosion on the lateral strength of joints. *For. Prod. J.* 62, 160–166. <https://doi.org/10.13073/0015-7473-62.3.160>.
- Leicester, R.H. (2001). Engineered durability for timber construction. *Prog. Struct. Eng. Mater.* 3, 216–227. <https://doi.org/10.1002/pse.72>.
- Zelinka, S.L., Glass, S.v., and Derome, D. (2014). The effect of moisture content on the corrosion of fasteners embedded in wood subjected to alkaline copper quaternary treatment. *Corros. Sci.* 83, 67–74. <https://doi.org/10.1016/j.corsci.2014.01.044>.

15. Zelinka, S.L., Rammer, D.R., and Stone, D.S. (2008). Electrochemical corrosion testing of fasteners in extracts of treated wood. *Corros. Sci.* 50, 1251–1257. <https://doi.org/10.1016/j.corsci.2007.12.006>.
16. Zelinka, S.L., Asce, S.M., Rammer, D.R., and Asce, M. (2009). Corrosion rates of fasteners in treated wood exposed to 100% relative humidity. *J. Mater. Civil Eng.* 21, 758–763. [https://doi.org/10.1061/\(asce\)0899-1561\(2009\)21:12\(758\)](https://doi.org/10.1061/(asce)0899-1561(2009)21:12(758)).
17. Zelinka, S.L., Passarini, L., Matt, F.J., and Kirker, G.T. (2019). Corrosiveness of thermally modified wood. *Forests* 11, 50. <https://doi.org/10.3390/f11010050>.
18. White, R. (2019). Metal and timber: making the right connections. In *TRADA's Timber 2019 Industry Yearbook*, pp. 218–219.
19. Boonstra, M.J., van Acker, J., Tjeerdsmā, B.F., and Kegel, E.v. (2007). Strength properties of thermally modified softwoods and its relation to polymeric structural wood constituents. *Ann. For. Sci.* 64, 679–690. <https://doi.org/10.1051/forest:2007048>.
20. Zhu, X., Gao, Y., Dai, Z., Corr, D.J., and Shah, S.P. (2018). Effect of interfacial transition zone on the Young's modulus of carbon nanofiber reinforced cement concrete. *Cem. Concr. Res.* 107, 49–63. <https://doi.org/10.1016/j.cemconres.2018.02.014>.
21. Haufe, J., and Vollpracht, A. (2019). Tensile strength of concrete exposed to sulfate attack. *Cem. Concr. Res.* 116, 81–88. <https://doi.org/10.1016/j.cemconres.2018.11.005>.
22. Shaikh, F.U.A. (2018). Effect of cracking on corrosion of steel in concrete. *Int. J. Concr. Struct. Mater.* 12, 3–12. <https://doi.org/10.1186/s40069-018-0234-y>.
23. Wang, Q., Cao, J., Liu, X., Yang, S., and Jiang, M. (2020). Self-healing coatings for inhibiting corrosion of ferrous metals exposed to preservative-treated bamboo. *J. Wood Sci.* 66, 1–10. <https://doi.org/10.1186/s10086-020-01865-4>.
24. Li, T., Song, J., Zhao, X., Yang, Z., Pastel, G., Xu, S., Jia, C., Dai, J., Chen, C., Gong, A., et al. (2018). Anisotropic, lightweight, strong, and super thermally insulating nanowood with naturally aligned nanocellulose. *Sci. Adv.* 4, eaar3724. <https://doi.org/10.1126/sciadv.aar3724>.
25. Kaplan, D. (1998). *Introduction to Biopolymers from Renewable Resources* (Springer), pp. 1–29.
26. Gaitán-Alvarez, J., Berrocal, A., Mantanis, G.I., Moya, R., and Araya, F. (2020). Acetylation of tropical hardwood species from forest plantations in Costa Rica: an FTIR spectroscopic analysis. *J. Wood Sci.* 66, 1–10.
27. Kubovský, I., Kačíková, D., and Kačík, F. (2020). Structural changes of oak wood main components caused by thermal modification. *Polymers* 12, 485. <https://doi.org/10.3390/polym12020485>.
28. Sundqvist, B., Karlsson, O., and Westermark, U. (2006). Determination of formic-acid and acetic acid concentrations formed during hydrothermal treatment of birch wood and its relation to colour, strength and hardness. *Wood Sci. Technol.* 40, 549–561. <https://doi.org/10.1007/s00226-006-0071-z>.
29. Yang, W.J., Yang, P., Li, X.M., and Feng, W.L. (2012). Influence of tensile stress on corrosion behaviour of high-strength galvanized steel bridge wires in simulated acid rain. *Mater. Corros.* 63, 401–407. <https://doi.org/10.1002/maco.201005921>.
30. Vera, R., Venegas, R., Carvajal, A.M., Corvo, F., and Pérez, T. (2012). Performance of carbon steel and galvanized steel in reinforced concrete structures after accelerated carbonation. *Int. J. Electrochem. Sci.* 7, 10722–10734.
31. Delahay, P., Pourbaix, M., and Van Rysselberghe, P. (1951). Potential-pH diagram of zinc and its applications to the study of zinc corrosion. *J. Electrochem. Soc.* 98, 101. <https://doi.org/10.1149/1.2778110>.
32. Xie, W., Li, J., and Li, Y. (2017). Electrochemical corrosion behavior of carbon steel and hot dip galvanized steel in simulated concrete solution with different pH values. *Medziagotyra* 23, 280–284. <https://doi.org/10.5755/j01.ms.23.3.16675>.
33. Stefanoni, M., Angst, U.M., and Elsener, B. (2019). Kinetics of electrochemical dissolution of metals in porous media. *Nat. Mater.* 18, 942–947. <https://doi.org/10.1038/s41563-019-0439-8>.
34. Li, T., Li, S.X., Kong, W., Chen, C., Hitz, E., Jia, C., Dai, J., Zhang, X., Briber, R., Siwy, Z., et al. (2019). A nanofluidic ion regulation membrane with aligned cellulose nanofibers. *Sci. Adv.* 5, eaau4238. <https://doi.org/10.1126/sciadv.aau4238>.

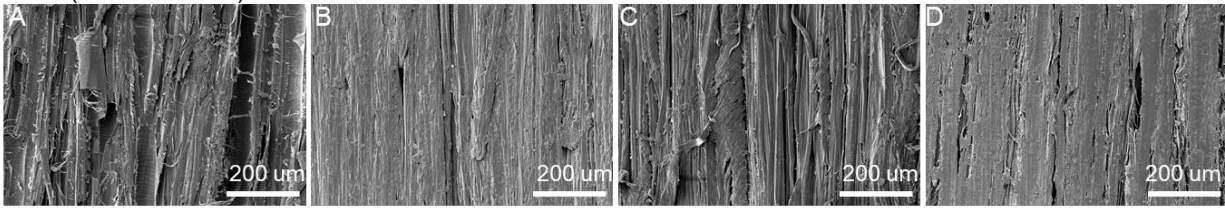
Cell Reports Physical Science, Volume 3

Supplemental information

A low-corrosivity structural timber

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SEM (non-densified)



SEM (densified)

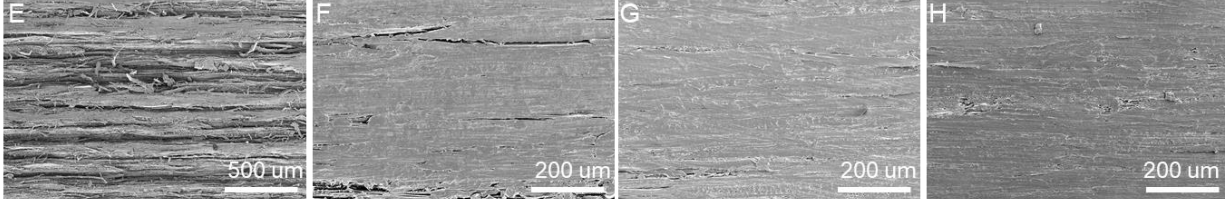


Figure S1. Cross-sectional morphology of basswood samples. (A) Natural basswood, (B) 4h-delignified wood, (C) 8h-delignified wood, (D) 12h-delignified wood, (E) Densified natural wood, (F) Densified 4h-delignified wood, (G) Densified 8h-delignified wood, and (H) Densified 12h-delignified wood.

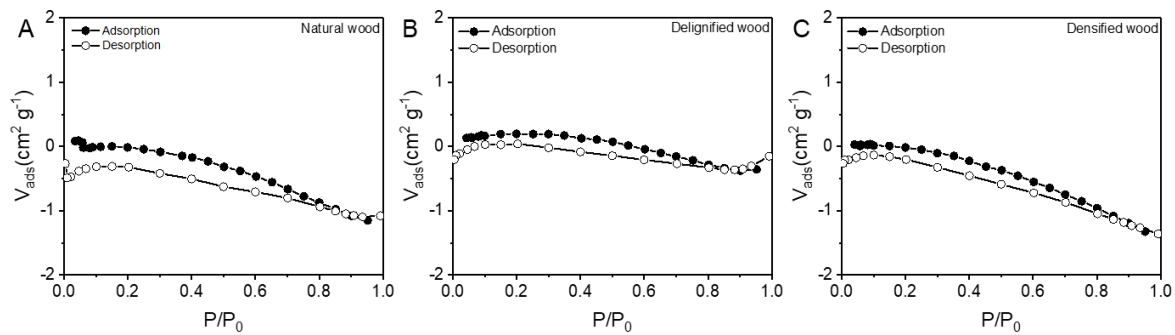


Figure S2. BET results of wood samples. (A) Natural wood, (B) delignified wood, and (C) densified wood. N_2 sorption at 77K.

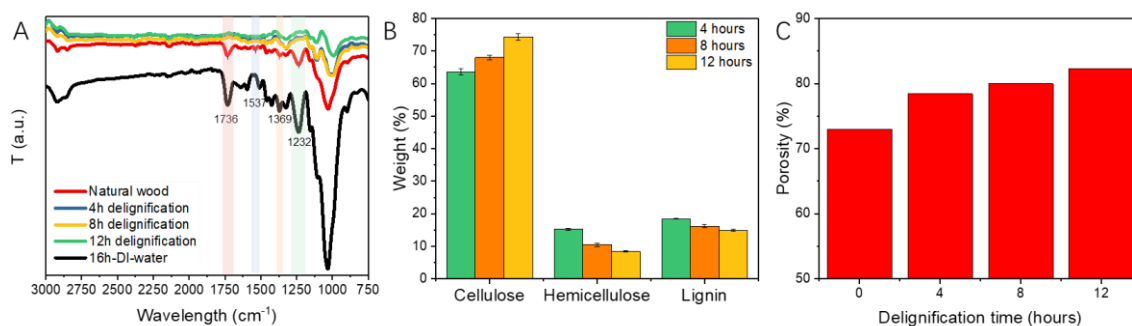


Figure S3. Wood characterizations. (A) IR spectra of natural basswood, delignified wood (delignification time: 4, 8, and 12 h) and basswood boiled with deionized water (DI-water) over 16 h. (B) Wood compositions and (C) porosities of delignified wood (delignification time: 4, 8, and 12 h). The error bars describe the ranges of three repeated data points.

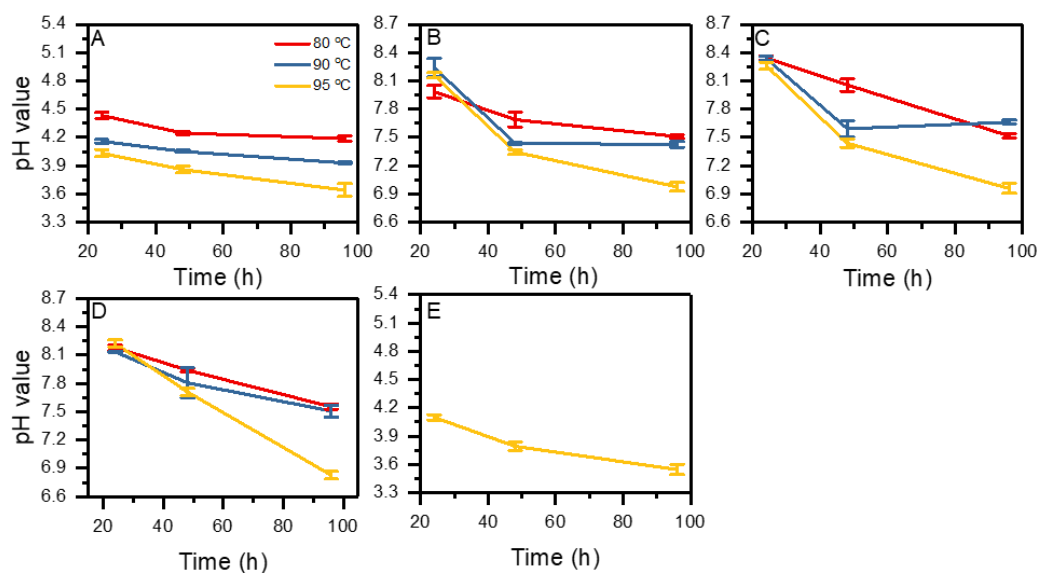


Figure S4. pH evaluation of basswood samples soaked in water. (A) Natural basswood, (B) 4h-delignified wood, (C) 8h-delignified wood, and (D) 12h-delignified wood at 80°C, 90°C, and 95°C, respectively. (E) Basswood (boiled in DI-water over 16 hours) evaluated at 95°C. The error bars describe the ranges of three repeated data points.

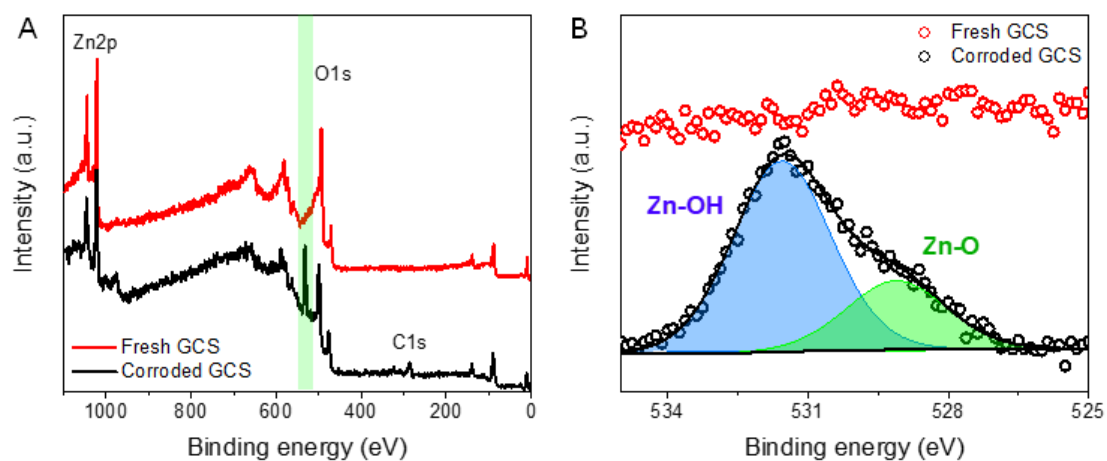


Figure S5. XPS analysis of corrosion products. (A) Survey and (B) O1s of fresh GCS and corroded GCS in densified wood. The O1s peaks of the corroded GCS represent the signals of Zn-OH and Zn-O.

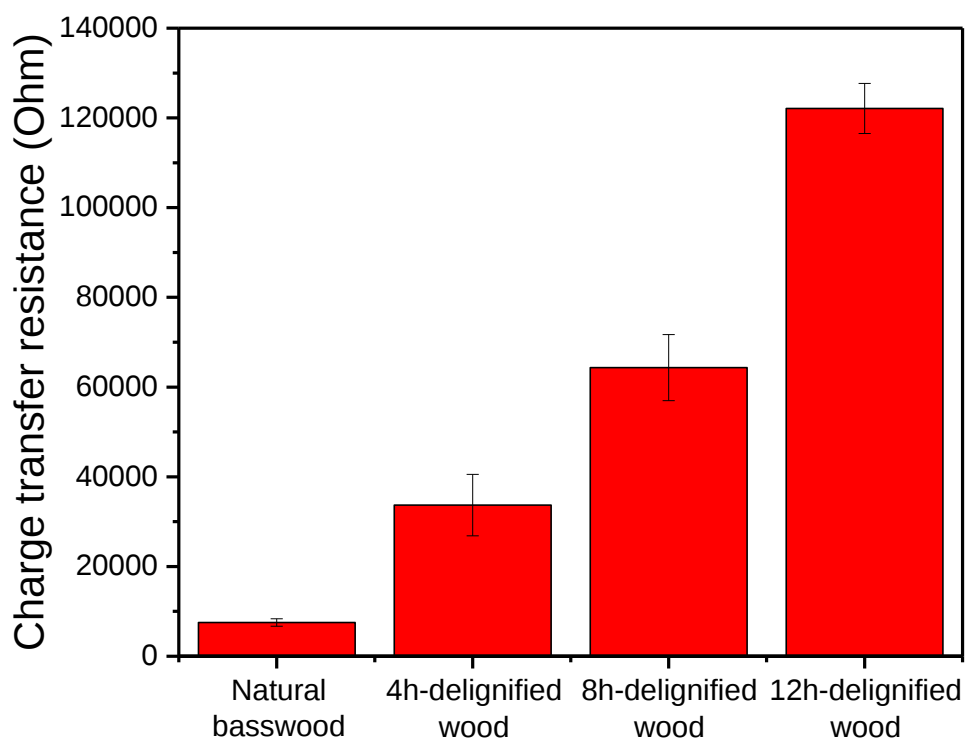


Figure S6. Charge transfer resistance evaluation. Charge transfer resistance of two galvanized low-carbon steel electrodes in natural basswood, 4h-delignified wood, 8h-delignified wood, and 12h-delignified wood extracts were obtained by EIS tests. The error bars describe the ranges of three repeated data points.

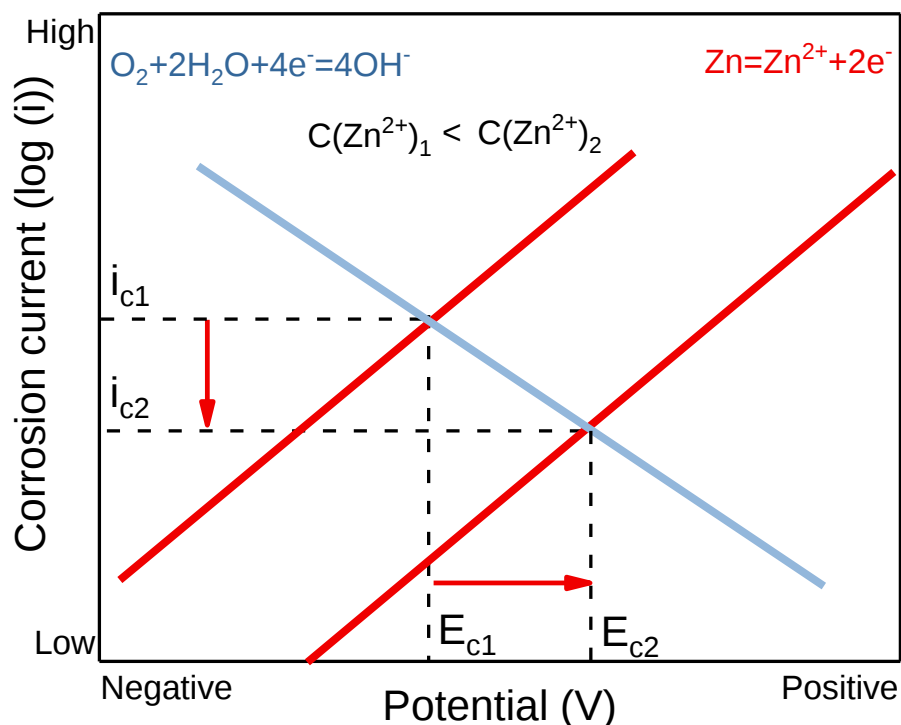


Figure S7. Evan's diagram. Blue line is the cathodic reaction (oxygen reduction) and red lines are the anodic reactions (zinc oxidation). The intersection of the blue and red line determines the corrosion rate i_c and the corrosion potential E_c . The reversible potential ($E_{Zn/Zn^{2+}}^{rev}$) of the red line can be described by the Nernst equation: $E_{Zn/Zn^{2+}}^{rev} = E_{Zn/Zn^{2+}}^o + \frac{RT}{2F} \ln(c(Zn^{2+}))$. Here, $E_{Zn/Zn^{2+}}^o$ is the standard potential. The dense wood structure impedes the mass transfer leading to a higher $c(Zn^{2+})$ at the Zn/wood interface. Hence, the reversible potential of Zn shifts to a more positive value leading to a more positive E_c and a lower corrosion rate (i_c) of GCS.

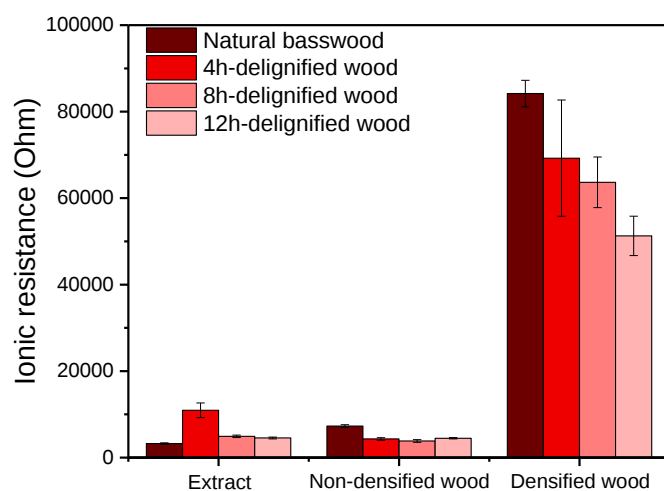


Figure S8. Ionic resistance evaluation. The ionic resistance values of natural basswood and delignified wood (4, 8, and 12 h) as well as their extract= solutions. For the test in wood extract, two electrodes were immersed in the solution that are one inch apart and parallel to each other. The error bars describe the ranges of three repeated data points.

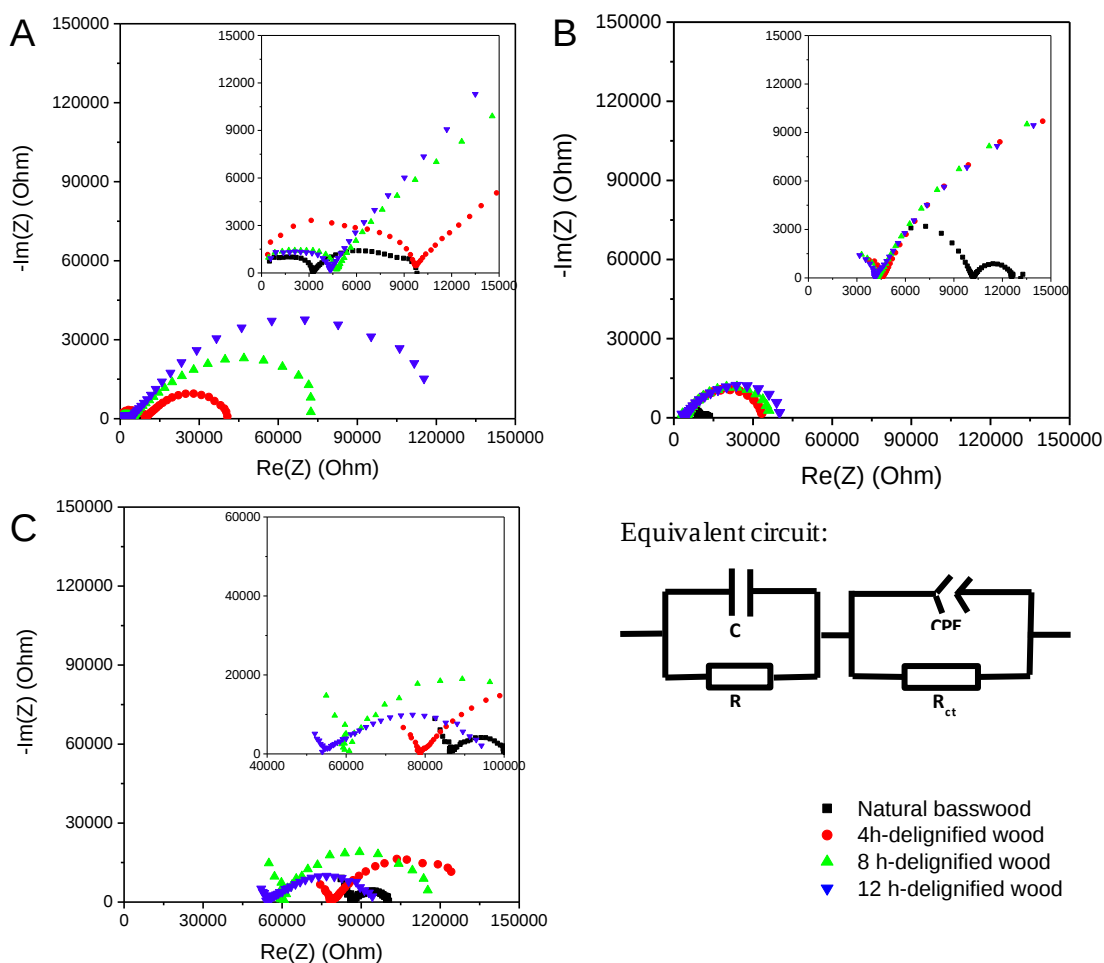


Figure S9. EIS test to measure charge transfer resistance and ionic conductivity. The EIS of natural basswood and delignified wood (4 h, 8 h, and 12 h) when sandwiched between two GCS sheets: (A) In the extract solution, (B) Non-densified wood and (C) Densified wood. EIS measurements were carried out in the frequency range of 7 MHz–0.1 Hz.

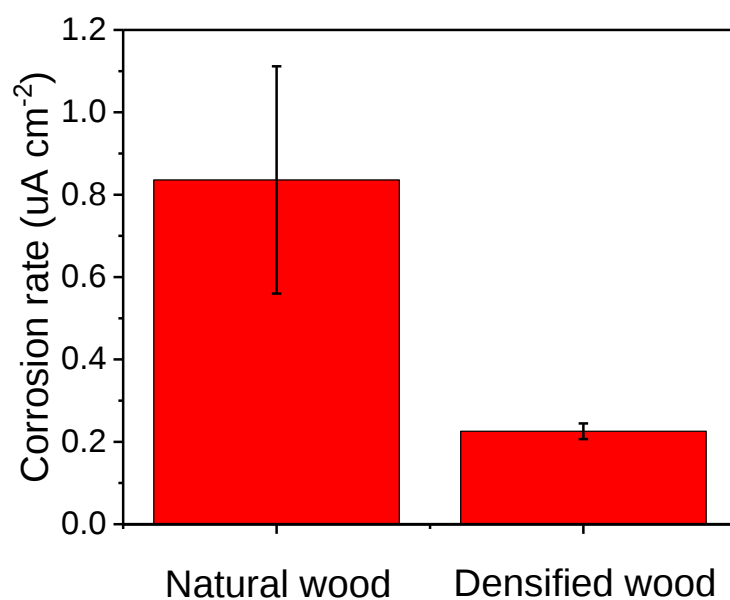


Figure S10. Long-term corrosion evaluation of GCS in wood. The long-term corrosion evaluation of GCS in natural wood and densified wood was evaluated by storing the metal-wood couple in a box with a relative humidity of 100% over one year. The unit is converted from $\text{mg cm}^{-2}\text{day}^{-1}$ to $\mu\text{A cm}^{-2}$. The error bars describe the ranges of three repeated data points.

Table S1. Experimental data for mathematical model. The density of wood samples was obtained by at least three repeated measurements. The corrosion rate measured with the wood extract can be regarded as the value for a wood sample with a porosity approaching 1. For extract, non-densified wood, and densified wood, the corrosion rate of each condition contains three repeats. For partially densified wood, the corrosion rate of each condition contains one repeat.

	Delignification time	Density	Porosity	Average corrosion rate	Relative standard deviations
	hour	g cm^{-3}		$\mu\text{A cm}^{-2}$	$\mu\text{A cm}^{-2}$
Extract	0	-	1	9.130	4.600
	4	-	1	0.981	0.723
	8	-	1	0.520	0.190
	12	-	1	0.611	0.345
Non-densified wood	0	0.400	0.733	1.310	0.594
	4	0.320	0.787	0.788	0.473
	8	0.300	0.800	0.776	0.435
	12	0.280	0.813	0.441	0.172
Partially densified wood (0.12 inch thick)	4	0.932	0.379	0.225	-
	8	0.767	0.489	0.260	-
	12	0.818	0.455	0.392	-
Partially densified wood (0.1 inch thick)	4	1.218	0.188	0.076	-
	8	1.046	0.303	0.109	-
	12	1.126	0.249	0.115	-
Densified wood (0.08 inch thick)	4	1.357	0.095	0.050	0.024
	8	1.354	0.097	0.090	0.034
	12	1.345	0.104	0.062	0.019