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Ion Transport in Thermally Responsive Pectin film

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The ionic conductivity of $CaCl_2$-crosslinked pectin was found to exhibit a record-high temperature response, suggesting its potential applications in wearable devices and infrared sensors[1]. However, little was known about its ion conduction mechanisms and the origin of its high-temperature sensitivity. In this study, we perform controlled experiments and identify calcium ions as the dominant current carriers. By analyzing infrared spectra at different temperatures, we find that the temperature response is due to changes in ion mobility, rather than variations in ion number density. We compare measurements and modeling results of 9 different multivalent ions and find a positive correlation between their temperature responses and their binding energy to pectin. While these findings are fundamental in nature, they provide relevant guidance for the future design of temperature-sensitive polymers and other materials for organic electronics.

Thermal sensing technologies have been developed for a wide range of applications including wearable devices, robotics, infrared sensing, and internet of things[2–4]. Recent reports discovered a new type of thermal sensing material[1]: $CaCl_2$-crosslinked pectin. Its electrical conductivity is highly sensitive to temperature changes, over a wide range of temperatures. Compared to the state-of-art temperature sensing materials, like vanadium oxide, pectin has been found to be at least an order of magnitude higher in its response[1]. Furthermore, pectin is transparent, solution processable, biodegradable, inexpensive, and lightweight, making it a great candidate for large-scale temperature mapping applications, such as electronic skins.

Pectin is a structural polysaccharide that can be extracted from plant cells. It has been frequently used in the food and pharmaceutical industry as gelling agents. It is polydisperse and has a complex structure[5]. The pectin backbone is mainly composed of homogalacturonan, rhamnogalacturonan I (RG I), and II (RG II). RG I and RG II with complicated side chains, making it difficult to understand the exact molecular structure[6]. However, homogalacturonan, which consists of at least 65% of the pectin molecule, is composed of a relatively simple linear chain of 1,4-linked α-d-galacturonic acids with C-6 carboxyl groups partially esterified[7]. When the degree of esterification is low, calcium ions can bind with carboxyl groups of the pectin chain resulting in the gelation of pectin solutions[8]. This binding interaction has been experimentally observed using Fourier Transform Infrared Spectroscopy (FTIR)[9,10]. Previous simulation studies also found that calcium ions can bind with carboxyl groups on the pectin chain to form an egg-box-like structure, as shown in Fig. 1. Some studies found that in a similar system, hydroxyl groups also participate in ion coordination. When water molecules are present, calcium ions are partially solvated by water[11,12]. Other divalent ions, such as copper and zinc ions, have also been shown to bind with pectin to different degrees[13].

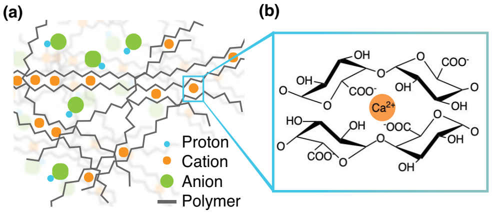

FIG. 1. (a) Schematic diagram showing divalent-cation crosslinked pectin. The divalent cations (orange) can deprotonate polygalacturonic acid and crosslink multiple polymer chains to form a connected network. The proton (light blue) disassociated from the galacturonic acid can form ion pairs with the anion (green) from the crosslinking salt, when the water content in the network is low. (b) Coordination between calcium ion and galacturonates.

In previous studies, it has been shown that the interaction between calcium chloride and pectin is essential to temperature sensitivity[1]. However, little is known about pectin's ion transport mechanisms and the origin of its temperature response. The lack of knowledge about the underlying molecular mechanisms governing petcin's temperature response hinders the optimization of this polyelectrolyte for sensing applications. Nevertheless, probing the ion transport mechanisms in this biopolymer is challenging. First of all, the composition and the structure of the RG section of pectin are extremely complicated and not well understood. This renders nuclear magnetic resonance spectroscopy and many other spectroscopic results noisy and hard to decipher. Secondly, multiple factors could affect the interaction between cations and pectin. Type of ions, pH, degree of acetylation, and distribution pattern of carboxyl groups all can have a great impact on the ion-pectin coordination geometry and pectin's binding capacity[14]. Thirdly, there are multiple types of mobile ions present in the system: calcium ions, chloride ions, and protons from carboxyl groups. They all could be contributing to the overall ionic current and temperature sensitivity.

This paper focuses on the identification of the dominant current carrier in pectin and elucidates the causes of its high-

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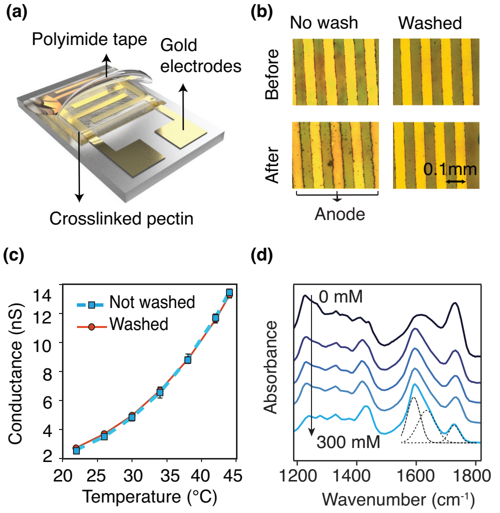

FIG. 2. (a)Schematic diagram of samples fabricated for electrical measurements. Pectin was deposited on the gold-interdigitated electrodes and then crosslinked with salt solutions. After dehydration, it was then sealed with polyimide tape. (b) Optical microscopy images of the gold interdigitated electrodes. The first (second) row corresponds to the electrodes before (after) the gold-dissolution electrochemical test. Compared to the first column, the sample measured using the electrodes in the second column was washed in deionized water before measurements. (c) The electrical properties of the washed sample (red circle) compared to the unwashed one (blue square). No significant difference was observed. The error bars are on the order of graph point size.(d) FTIR spectra of pectin crosslinked with 5 concentrations of $CaCl_2$: 0, 30, 80, 100, 300 mM. Dotted lines correspond to three fitted Gaussian peaks to the spectrum of pectin cross-linked with 300 mM $CaCl_2$ between 1550 cm^{-1} and 1800 cm^{-1}.

temperature sensitivity. By comparing electrical responses of systems with different amounts of chloride ions and protons, we found that calcium ions are the main current carrier in $CaCl_2$-crosslinked pectin. To understand the origin of the temperature sensitivity, we studied the electrical responses of pectin films crosslinked with nine types of multi-valent ions. Binding interactions between these ions and pectin were also investigated via infrared spectroscopy and density functional theory modeling. Combining these results, we conclude that the temperature sensitivity is correlated to the binding energy between the metal ion and pectin.

First, we identified the main charge carrier responsible for the large temperature response. Three types of mobile ions present in the system were considered : (i) calcium ions, (ii) chloride ions, and (iii) protons from the carboxyl group. Assuming ideal electrolytes, the ion conductivity could be written as the sum of contributions from all mobile ions:

$$\sigma(T) = \sum_i \sigma_i(T) = \sum_i n_i(T)\mu_i(T)q_i \tag{1}$$

where n_i,μ_i, and q_i are the number density, the mobility, and the charge of the i-th type of mobile ions. T refers to the temperature. In general, both number densities and mobilities can depend on temperature, and the temperature response in this paper is defined as $\sigma(T_1)/\sigma(T_2)$ where $T_1 > T_2$. If protons are the dominant current carriers, then the temperature response of $CaCl_2$-crosslinked pectin should be similar to the uncrosslinked pectin, where protons are the only possible current carrier. However, previous studies found that the temperature response of uncrosslinked pectin films is less than 1/4th of the temperature response of $CaCl_2$-crosslinked pectin[1]. To further separate the contribution of (i) calcium ions from (ii) chloride ions and (iii) protons, we performed controlled experiments comparing the electrical properties of samples containing two different concentrations of chloride ions and protons. Pectin solution was drop casted on the gold electrodes (Fig. 2 (a)) and then crosslinked with $CaCl_2$ solution (see the supplementary material for more details). One sample was immersed in DI water for a day to remove the chlorides and unbound protons. Calcium ions that deprotonated the carboxylic acid groups formed strong coordination with the negatively charged carboxylate groups that remained during the DI rinse. Both samples were dehydrated and subjected to a gold-dissolution electrochemical test (Fig. 2b). By applying 1 V of voltage to the pectin-deposited electrodes for 7 hours at room temperature, the surface of the gold anode was monitored. As expected, the unwashed samples turned red due to the formation of auric chloride from the reaction between gold and chloride ions in the acidic environment[15], while no color change was observed from the DI rinsed samples. This confirmed that the rinsed pectin film contained significantly fewer chloride ions. Moreover, since this system must be electrically neutral after rinsing, the same number of protons must have been removed. Finally, the electrical responses of both rinsed and unrinsed samples were characterized by procedures described in the supplementary material. Their electrical conductance at varying temperatures is plotted in Fig. 2c. No significant difference in the electrical response was observed, suggesting that chloride ions and protons are not the dominant current carriers that cause the high-temperature response in the system.

Although we confirmed that calcium ions play an important role in pectin's high-temperature response, questions remain on what mechanisms gives rise to pectin's high-temperature response. Both the number density and the mobility of the current carriers could be temperature dependent and contribute to the thermal response. We first inspect the possibility of the charge carrier density being responsible for the pectin's temperature response. In general, the number density of unbound calcium ions is expected to increase with increasing temperature[16]. Since these unbound calcium ions are much more mobile than the bound calcium ions, the number density would be expected to increase, leading to higher conductivity. To test such hypothesis, we monitored how the

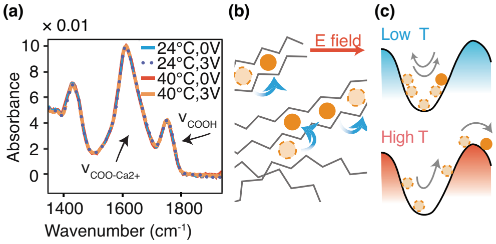

FIG. 3. (a) Infrared spectra of $CaCl_2$ crosslinked pectin film taken at 24 °C, with no voltage (light blue), 24 °C with 3 volts applied across the sample (dotted dark blue), 40°C with no voltage (red) and 40 °C with 3 volts applied across the sample (orange)the red line. (b) Schematic illustration showing how calcium ions hop from one solvation site to another in pectin chains. (c) Schematic showing the free energy surface for a calcium ion at a solvation site and its hopping activation energy E_A.

number density of the bound calcium ions changes with respect to the applied voltage and temperature using infrared (IR) spectra. Three major absorption peaks were present from the crosslinked pectin in the range between 1500 cm^{-1} and 1800 cm^{-1}: Each corresponded to the asymmetric stretch of the carboxyl group (1733 cm^{-1}), the asymmetric stretch of the metal-ion-bound carboxylate group (1593 cm^{-1}), and the scissoring bend of the water molecules (1620 cm^{-1})[9,10]. As shown in Fig. 2(d), with increasing concentration of crosslinking $CaCl_2$, the peak corresponding to the metal-ion-bound carboxylate group rises while the peak corresponding to the carboxyl group diminishes. Therefore, the concentration of bound calcium ions could be measured using IR spectra. Interestingly, all four IR spectra of the $CaCl_2$ crosslinked pectin that were measured under different temperatures and conditions overlapped (Fig. 3a), suggesting that no significant change in the number density of bound/free calcium ions had occurred. Therefore, we can conclude that pectin's thermal response originates from the change in ion mobility.

We postulate that the steep dependence of ion mobility on temperature arises from the strong binding strength between the calcium ions and pectin. With an applied electric field (Fig. 3b), bound calcium ions can hop to another site by crossing energy barriers (Fig. 3c). At elevated temperatures, this hopping frequency increases due to an increase in thermal energy resulting in a higher ion mobility and ion conductivity. Such phenomenon can be explained using the Arrhenius theory[17,18]. To verify our claim, the electrical properties and binding strengths of pectin samples crosslinked with different multivalent salts were evaluated.

For electrical characterizations, we prepared samples crosslinked with 9 multivalent salts solution with the same concentration 30 mM: $CaCl_2$, $CuCl_2$, $FeCl_2$, $FeCl_3$, $BaCl_2$, $CoCl_2$, $ZnCl_2$, $AlCl_3$ and $MgCl_2$. Each sample was deposited on the electrode surfaces. We applied a 100 mV step voltage and measured the current as a function of time. The ionic current value was extracted from the time-independent plateau region (before the charge polarization was fully developed)[19]. The temperature was cycled from 18 °C to 47 °C. The temperature response is defined as $\sigma_{45°C}/\sigma_{20°C} = I_{45°C}/I_{20°C}$, where $\sigma_{45°C}$, $\sigma_{20°C}$, $I_{45°C}$, and $I_{20°C}$ are the electrical conductivity and electrical current magnitude at 45°C and 20°C, respectively. From the temperature responses measured over different cross-linking salts (Fig. 4a), we observed that the temperature response is highly dependent on the type of crosslinking metal ion, providing additional evidence to our previous conclusion that metal ions are the dominating current carriers. Also, copper shows the highest response value compared to other ions. However, no apparent trend was recognized between the temperature response and the size of ions or their valency. Nevertheless, all samples followed the Arrhenius relation: $I = I_o exp(-E_A/k_B T)$, where E_A is the activation energy for hopping, k_B is the Boltzmann constant, and T is the temperature, and I_0 is the pre-exponential factor respectively (Fig. 4b). Such ion transport behavior in polymeric systems indicates independent ion hopping, without coupling with the polymer chains' segmental motion[17,20]. Finally, the activation energy from each ion was extracted (Fig. 4d). Since the response is defined as a current ratio, temperature responses are exponentially dependent on activation energies.

To characterize and compare the affinity of ions to pectin, binding curves of $CuCl_2$, $CaCl_2$, $FeCl_2$, and $MgCl_2$ crosslinked pectin were measured using infrared spectroscopy (Fig. 4c). Binding curves explain how the percentage of bound metal ions (i.e., the binding ratio) change with the concentration of the crosslinking solution. To obtain the binding ratios, Gaussian peaks were fitted to each FTIR spectrum between 1500 cm^{-1} and 1850 cm^{-1} (Fig.4c). For simple reactions, i.e. $M + L \rightleftharpoons ML$, and independent binding events, the dissociation constant K_d equals to the corresponding [L] when f_{ratio}=0.5[21]. In these cases, the binding constant $K_a = 1/K_d$ and binding free energy $\Delta G = -k_B T ln K_a$ can be calculated easily. In the metal crosslinked pectin system, the binding process could be more complicated, including multiple binding steps and correlations between adjacent binding sites. However, to qualitatively compare the binding affinity between different ions, we use $[L]_{f=0.5}$ as an estimate of K_d[22]. We found that the binding affinity decreases as follows: $Cu^{2+} > Fe^{2+} \geq Ca^{2+} \gg Mg^{2+}$ (Fig.4(c)). This order matches their corresponding order in temperature responses.

For further evaluation, binding energies between divalent ions and galacturonate were calculated using density functional theory (DFT) with ORCA package[23](see the supplementary material for more details). For each calculation, a negatively-charged galacturonate molecule, a metal ion, and 6 water molecules were included in the simulation. Finally, the binding energy was estimated using the following equation[24]:

$$\Delta E = E_{Gal^- M^{2+} \cdot 6H_2O} - E_{Gal^- \cdot 6H_2O} - E_{M^{2+}}, \qquad (2)$$

where $E_{Gal^- M^{2+} \cdot 6H_2O}$ corresponds to the energy of the optimized galacturonate-metal-ion-water complex. $E_{Gal^- \cdot 6H_2O}$ is the single point energy of $Gal^- \cdot 6H_2O$ calculated at the optimized geometry of $Gal^- M^{2+} \cdot 6H_2O$. To confirm whether our model can properly represent the binding interaction between the metal ions and pectin in the metal-ion-crosslinked

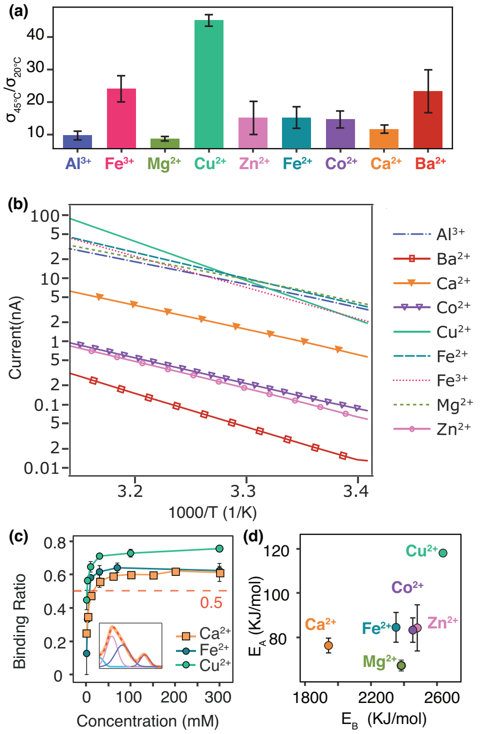

FIG. 4. (a) Temperature responses of pectin samples crosslinked by 9 different multivalent ions. Error bars are the standard deviations of at least 3 independent samples. The salts are ordered such that the ion size increases from left to right. (b) Arrhenius plots of pectin films crosslinked by the 9 different multivalent cations. Slopes of fitted lines are summarized in Table S1. The symbols used in the curves serve only to distinguish between different curves and are not indicative of data points. (c) Binding curves for Ca^{2+}, Fe^{2+} and Cu^{2+}. The inset shows a typical fitting of a FTIR with 4 Gaussian peaks (shown as cyan, pink, blue and purple curves). The red dashed line corresponds to the overall fitting, and the yellow curve is the experimentally measured absorption data. (d) Activation energy E_A is compared with the binding energy E_B obtained from DFT computation. The error bar for the copper ion is smaller than the graph point size.

pectin system, frequency calculations were performed to generate the corresponding infrared spectra. The calculated spectra showed qualitative agreement with experimental results regarding the locations of symmetric and antisymmetric vibration peaks of the metal-bound carboxylate group, at around 1420 cm^{-1} and 1590 cm^{-1}, respectively[25] (FIG. S1(a)). In the region below 1500 cm^{-1}, called the "fingerprint region" for polysaccharides, many peaks that correspond to glycosidic linkage vibration are not present in the simulated spectra, because only one monomer is included in the DFT calculation[9]. In the region above 1500 cm^{-1}, peaks corresponding to metal-bound carboxylate groups and water were observed in both IR spectra. The concentration ratio of these molecules used in the DFT calculation does not necessarily match the one observed experimentally, and thus, the relative peak heights are not expected to agree quantitatively. Due to the relativistic quantum effect that was not implemented in our calculation, the binding energy calculated from barium ions was inaccurate and excluded from the comparison[26]. Figure 4d shows the binding energies between metal ions and galacturonate E$_A$ obtained from the DFT simulations, plotted against the activation energies E$_B$ extracted from the Arrhenius plots in Fig. 4b. Overall, a positive correlation was observed. However, compared to Ca^{2+}, Mg^{2+} showed surprisingly high binding energy with galacturonate, a result not observed in our experiments. This incongruity between experiments and numerical results is due to the high affinity of Mg^{2+} to water molecules. Earlier studies also found that Mg^{2+} has a much higher binding affinity to polygalacturonate than Ca^{2+}[13]. However, Mg^{2+} only polycondensates on polygalacturonic acid instead of crosslinking, because it is energetically unfavorable for Mg^{2+} to release water molecules from its solvation shell to bind with galactronate[13]. In our simulations, no ions bind with the hydroxyl group on the galacturonate molecule. This is because only one galacturonate molecule was included in the model, and it was sterically hindered for an ion to bind to both the carboxylate and hydroxyl groups. However, metal ions do coordinate with the hydroxyl groups in water molecules. With more galaturonate molecules present in the simulations, metal ions would also likely bind to the hydroxyl groups from other galacturonate molecules, as observed in other similar systems[12]. Considering the positive correlation observed between the activation and binding energies, from both experimental and simulation results, we conclude that the highly temperature dependent ion conductivity originates from the tight binding between calcium ion and pectin. Similar results were also demonstrated in a recent report, describing a polyelectrolyte similar to pectin, composed of 2-hydroxyethyl acrylate (HEA) and acrylic acid (AA)[27]. These findings further confirmed that the binding of calcium ions to carboxyl groups and hydroxyl groups is key to achieving high responsivity.

In this study, we elucidate the ion transport mechanism in dehydrated calcium pectinate. We identify calcium ions as the main current carrier of the system, and determine that conductivity is dominated by ion hopping, which is independent from the polymer segmental relaxation. We also demonstrate that the temperature dependency originates from changes in charge carrier mobility, rather than its number density. In addition, we show that the high activation energy is related to the strong binding between cation and galacturonate, specifically the carboxyl and hydroxyl groups. Finally, we highlight that Cu^{2+} cross-linked pectin is three-times more temperature responsive than Ca^{2+} cross-linked pectin, and therefore, the use of copper pectinate can significantly improve the thermal sensing performance for future developments and applications.

SUPPLEMENTARY

See supplementary material for additional details on the sample fabrication, electrical measurements, infrared spectroscopy, and DFT calculation.

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DATA AVAILABILITY STATEMENT

Most of the data supporting the findings of this study are available within the paper. Additional data are available from the corresponding author upon request.

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