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Dielectric processes of wet and well-dried wheat starch

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Abstract

The influences on polymer dynamics due to the presence of water molecules in dried wheat starch were studied by means of dielectric relaxation spectroscopy. The dominant relaxation process in the low temperature range due to a local motion of chain segments via the glycosidic linkages largely affected by the introduction of water molecules. Two relaxation processes called as β- and β_{wet}- in polymeric system in wet wheat starch were observed while no β_{wet}-relaxation was observed in well-dried wheat starch. We observed a higher dc contribution in presence of water molecules in the system. The shape and the intensity of β-relaxation were largely affected by introducing excess water molecules in wheat starch (wet state) in comparison with well dried sample. The activation energy of β-relaxation was increased in wet sample. An excess transition was observed in wet sample at ca. 30 °C. Such transition may be an inter-crystalline transition.

Keywords: Wheat starch; Dielectric relaxation; Transition

1. Introduction

Polysaccharide is a kind of long chain molecular system and also contains high polar molecular structures. Those molecules should exhibit dielectric behavior. Gelatinization creates a change in organization of the granules as a function of temperature and water content. Waigh, Gidley, Komanshek, and Donald (2000) indicates an analogy relating to the process of gelatinization. It was reported earlier (Meißner, Einfeldt, & Kwasniewski, 2000; Montes & Canaille, 1999) that the electronic characteristics of polysaccharides could be changed drastically by adding only small amounts of water. The dielectric relaxation spectroscopy is one of the unique method to investigate the changes within the molecular dynamics of polysaccharides influenced by interaction of polysaccharides with water molecules (van den Berg, 1981; Butler & Cameron, 2000; Cameron & Donald, 1993; Einfeldt, Meißner, & Kwasniewski, 2000; Einfeldt, Meißner, & Kwasniewski, 2003; Einfeldt, Meißner, Kwasniewski, & Einfeldt, 2001; H. Hatakeyama & T. Hatakeyama, 1998; Marcus, 1995).

Since, starch possessing the anhydro glucose unit (AGU) bearing dipolar side groups in their polymer backbone strongly interacts with water molecules a dipole–dipole interaction is expected to be occurred in wet wheat starch, that may largely affect the relaxation phenomena by introduction of water molecules in wheat starch. In our work, we are going to study such behavior. In the reported literatures, till now, five distinct relaxations, β-, γ-, β_{wet}-, δ- and σ-relaxations were found under several experimental conditions of polysaccharides molecules. We are going to connect all observed relaxation phenomena in our works with reported literatures. Finally, the effect of relaxation phenomena observed by introducing water molecules in wheat starch.

2. Experimental procedure

Wheat starch was used in this paper as a sample. The sample was used without additional purification and simply dried for 24 h under vacuum at 105 °C. In other occasion (for wet sample), the state resulting from storage of polysaccharides under normal air conditions contained ca. 12–13% water. The sample was collected from

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Prof. W. Flamme, Institut für Stressphysiologie und Rohstoffqualität Groß Lüsewitz, Germany. The sample was blocked from electrodes by thin Teflon sheets of approximately 0.03 mm thick. A measuring screw determined the sample thickness is of approximately 0.42 mm. The complex dielectric constant was measured in the frequency range from 10 mHz to 10 MHz by using the NOVOCONTROL Broadband Dielectric Spectrometer System BDS 4000 with the active sample cell BDC-S with the application of $1V_{pp}$ ac measuring field. By using Havriliak–Negami (H–N) fitting function (Havriliak & Negami, 1966) for multiple relaxation processes, the dielectric strength, relaxation time and relaxation frequency were estimated including the contribution that came from dc conductivity by using the following equation

$$\varepsilon^*(T) = \sum_{i=1}^{n} \frac{\Delta\varepsilon_i}{[1+(i\omega\tau_i)^{\alpha_i}]^{\beta_i}} + i\frac{S}{\omega^N} \tag{1}$$

where α_i and β_i are shape parameters of the relaxation processes (α_i is the width of relaxation process and β_i is the asymmetry of this process). τ_i is the relaxation time, $\Delta\varepsilon_i$ corresponds to the dielectric strength. All the above parameters are functions of temperature T.

The component form of Eq. (1) can be written as

$$\varepsilon'(T) = \mathrm{Re}\sum_{i=1}^{n} \frac{\Delta\varepsilon_i}{[1+(i\omega\tau_i)^{\alpha_i}]^{\beta_i}} \tag{2}$$

$$\varepsilon''(T) = \mathrm{Im}\sum_{i=1}^{n} \frac{\Delta\varepsilon_i}{[1+(i\omega\tau_i)^{\alpha_i}]^{\beta_i}} + \frac{S}{\omega^N} \tag{3}$$

where $\varepsilon'(T)$ and $\varepsilon''(T)$ are dielectric constant and dielectric loss, respectively, at T K.

The Arrhenius law of relaxation time can be written as

$$\tau(T) = \tau_0 \exp\{E_a/RT\} \tag{4}$$

where τ_0 is the pre-exponential factor. By plotting logarithmic $\tau(T)$ vs. $1000/T$, we calculated the molar activation energy (E_a) according to Arrhenius law (Eq. (4)) in different cases.

The pre-exponential factor τ_0 associated with the entropic effect S_a of the reorientation dynamics (Starkweather, 1991) by the following equation

$$-R\log\{\tau_D/\tau_0) \approx S_a \tag{5}$$

where $\tau_D = 1.76\times10^{-13}$ s is the Debye relaxation time at 0 °C; $T_0 = 273.15$ K. A comparison of the pre-exponential relaxation time τ_0 with the Debye relaxation time τ_D yields the entropy effect in the dielectric orientation relaxation. High values of S_a or low τ_0-values in comparison with τ_D can be interpreted as cooperative effect in the orientation motion of dipolar groups in the sample.

3. Results and discussion

We measured, experimentally, dielectric constant and loss of wheat starch in the dried state and wet state in the frequency range from 10^{-2} to 10^7 Hz. Figs. 1a,b and 2a,b shows the dielectric constant and loss spectra of the dried and wet state, respectively, at 20 °C.

It was observed experimentally that the dielectric constant at higher temperatures in both occasions is relatively high. Because of higher heat energy (kT) at high temperatures loosen the binding forces among AGUs. As a result, the orientation of the molecules on average is enable to orient in the direction of applied field either up or down much at higher temperatures at the cost of equal amount of electrical energy. The dielectric constant and loss factor were fitted using HN fitting functions separately. Since in the experiment, electrodes was blocked by Teflon non-conducting sheets, no electrode polarization or minimum electrode polarization is expected. At lower frequencies, the Maxwell–Wagner–Sillars (MWS) relaxation was occurred specially at high temperatures.

By taking into consideration of MWS relaxation at all temperatures for both systems HN fittings were done. At 20 °C in both occasions, two distinct relaxations were observed except MWS relaxation and fitted. A relaxation of

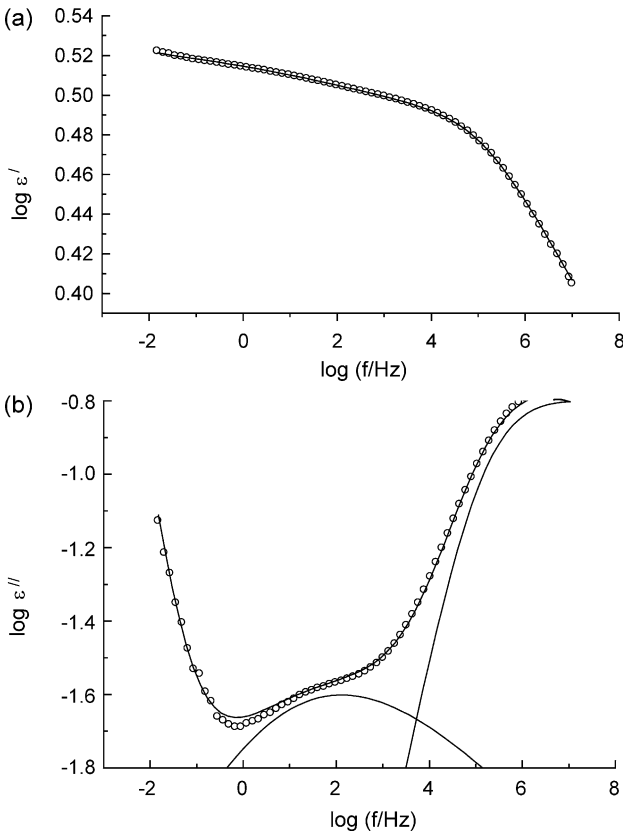

Fig. 1. Dielectric constant (ε') (Eq. (2)) (a) and dielectric loss (ε'') (Eq. (3)) (b) of dried wheat starch at 20 °C. The sample dried for 50 h at 105 °C in vacuum. The symbols are experimental points and the line is HN-fitting curve.

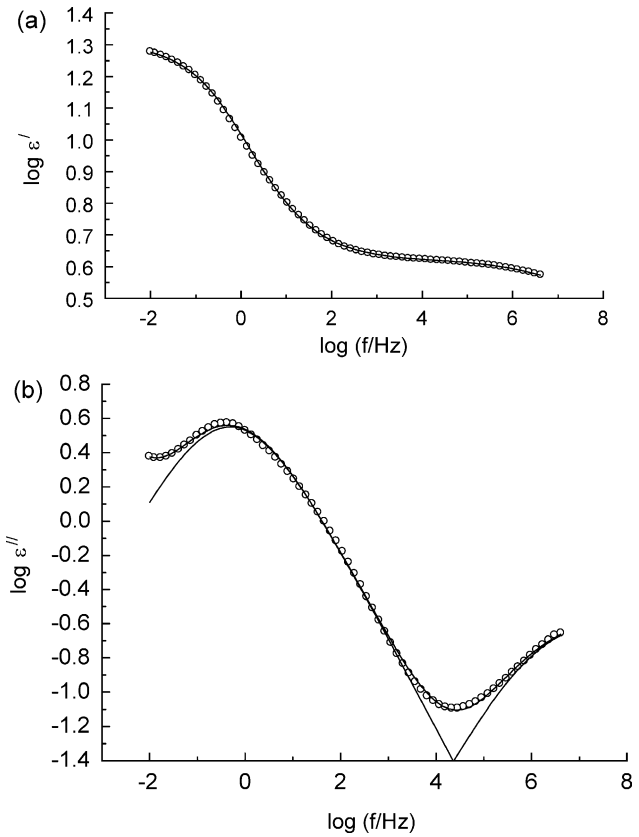

Fig. 2. Dielectric constant (ε') (Eq. (2)) (a) and dielectric loss (ε'') (Eq. (3)) (b) of wet wheat starch at 20 °C with 12–13% (w/w) water content. The symbols are experimental points and the line is HN-fitting curve.

very low frequency was observed at higher temperature in comparison with lower temperature. A high dc contribution on and above 20 °C was due to the mobility of ions at higher temperatures which is clearly shown in Fig. 3. In the case of wet sample, the molecules are also freely arranged at higher temperature than in lower temperature, so that same amount of energy could be able to orient molecules higher on average along the direction of applied field (Fig. 2a). In such case, a high dc contribution on and above − 15 °C arose due to the mobility of ions at higher temperatures in comparison with lower temperatures (Fig. 2b). Since Teflon sheets blocked the electrodes on both sides the electrode polarization did not occur. The blocking Teflon sheet enable to make the system uniformly distributed of charges with the application of external electric field. The MWS relaxation occurred at very lower frequency region. It has a large contribution to the relaxation processes at higher temperatures. We observed two transitions occur in wet sample at 60 and 30 °C (Fig. 4). Those two transition could be detected from the variation of dielectric constant (ε') with temperature at a constant frequency of 10 Hz and even at 10^4 Hz constant frequency. At 10^4 Hz fixed frequency, MWS relaxation and any other surface polarization should have very little (negligibly small) contribution to the dielectric constant. It simply concludes that (Fig. 4), at 60 °C and 30 °C two transitions definitely occurred. But, at present, we are unable to define those transitions appropriately.

It may be possible that an intermediate phase occurs at 30 °C transition that may be created due to the dipole–dipole interactions between water molecules and AGU. The detailed study is in progress.

The dielectric constant in wet sample is higher than that in dried sample because of higher dipole moment in wet sample due to the influenced of polar water molecules interaction with wheat starch. The dielectric strength of dried sample is less than that of wet sample at all relaxation processes (Figs. 5b and 6b). This is due to the ability of water to act as plasticizer.

Fig. 3 representing the loss factor due to dc conductivity alone, after deduction of loss contributed from all relaxation processes including MWS-relaxation, calculated by using S/ω^N in Eq. (3) after non-linear fitting (H–N) of the total loss factor. In wet sample, dc loss factor above ca. 55 °C, rises sharply with the increase of temperature, that is,

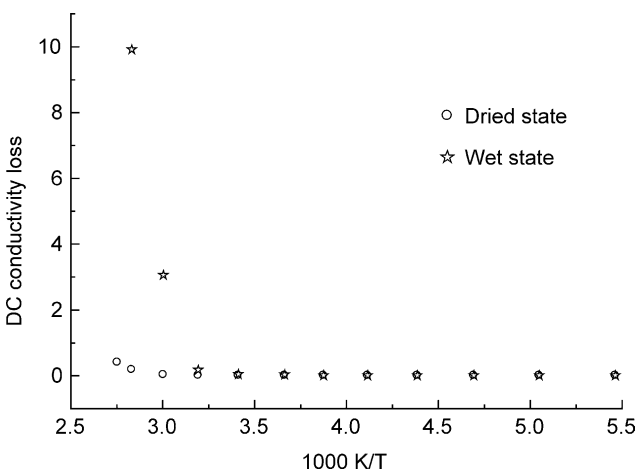

Fig. 3. Variation of dc-conductivity loss with temperature at 1 Hz.

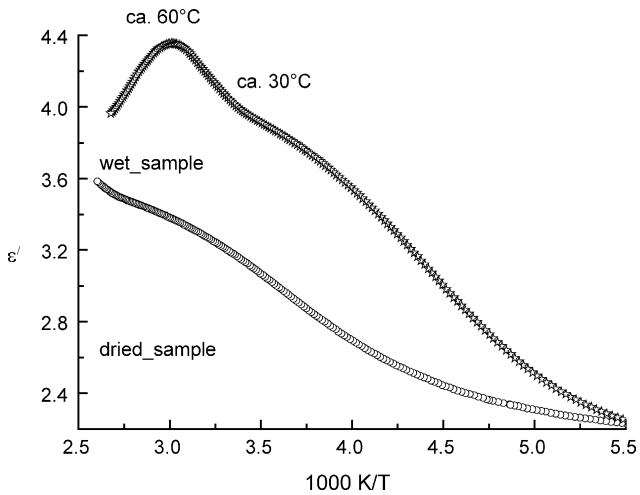

Fig. 4. Variation of dielectric constant (ε') with temperature at 10^4 Hz.

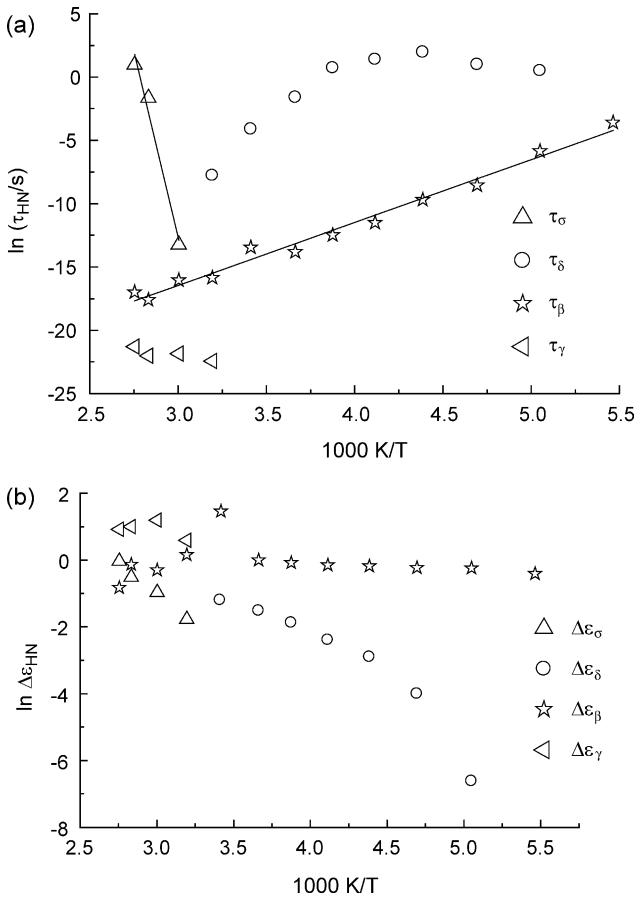

Fig. 5. (a) Variation of relaxation times (τ) for all dielectric relaxation processes found in well-dried wheat starch (Fig. 1a and b) with temperature. (b) Variation of dielectric strength ($\Delta\varepsilon$) with temperature for well-dried wheat starch.

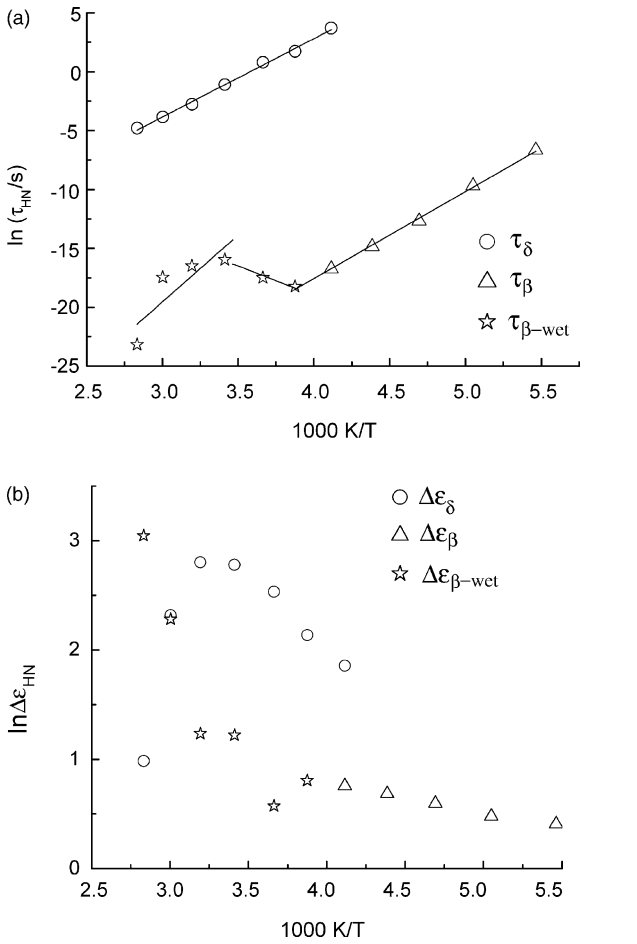

Fig. 6. (a) Variation of relaxation times (τ) for all dielectric relaxation processes found in wet wheat starch (Fig. 2a and b) with temperature. (b) Variation of dielectric strength ($\Delta\varepsilon$) with temperature for wet wheat starch.

because of higher temperature induces higher polarization of the system containing dipolar water molecules.

It was very difficult to separate all relaxations such as dc-conductivity, MWS-relaxation, σ-, δ-, β_{wet}-, β- and γ-relaxations, accurately, because of molecules have high electrical conductivity. However, we roughly estimated all fitting parameters (S, N, τ_i, $\Delta\varepsilon_i$, α_i and β_i) and dc-conductivity (S,N), and of σ-, δ-, β_{wet}-, β- and γ-relaxations by using component forms of HN- fitting functions (Eqs. (2) and (3)). In the dried samples, four distinct relaxations such as σ-, δ-, β- and γ-relaxations, can be assigned (Fig. 5a and b). In wet samples, three distinct relaxations such as δ-, β_{wet}- and β- relaxations can be assigned (Fig. 6a and b).

We observed a low frequency relaxation in dried sample (Fig. 5a and b). That relaxation is shifted continuously to lower frequencies if the temperature increases from 60 °C. Since the concept of 'random potential model' by Stevels (1957) and Taylor (1956) and the 'conducting path model' by Yamamoto and Namikawa (1988) and Namikawa (1975) can be useful for the interpretation of the σ-relaxation observed at high temperatures for polysaccharides with very low water content (2–3%) when the conductivity of this material cannot be neglected and because, our dried wheat starch system should expectedly have very low water residues that cannot be removed, the process can be assigned as σ-relaxation starting at 60 °C in higher temperature region in dried samples, which corresponds with the formation of dipolar structures in the material. That σ-process was not present in wet sample, because creation of a large number of free space charges simply dominates at low frequency region. The very high dc-conductivity and any polarization of space charges make unable to detect σ-relaxation process with water content 12–13% (w/w).

In comparison with the two papers (Einfeldt, Meißner, & Kwasniewski, 2003; Meißner, Einfeldt, & Kwasniewski, 2000), a δ-relaxation was observed in both occasions. In case of dried sample: the relaxation time (τ_δ) or relaxation frequency (f_δ) shows non-linear behavior with temperatures and extending from −90 to 40 °C. The relaxation frequency (f_δ) increases with increase of temperature. Dielectric strength ($\Delta\varepsilon_\delta$) also increases with the increase of temperature. In the case of wet sample: the relaxation time (τ_δ) or relaxation frequency (f_δ) shows non-linear behavior

with temperatures extending from −30 to 80 °C. The relaxation frequency (f_δ) increases with increase of temperature. Dielectric strength ($\Delta\varepsilon_\delta$) also increases with the increase of temperature and then decreases from 40 °C with the increase of temperature. The strength of this relaxation in wet sample is very high in comparison with that of dried sample.

The dielectric spectra of wet sample shows a higher strength throughout the temperature region. The β-process was largely affected by adding water molecules in the dried sample. The dielectric spectra are sorting the molecular units themselves by their relaxation time for reorientation in an electric field. The relaxation time of orientation motion is affected by the local environment of the molecular group (structure, morphology). Therefore, adding water dipolar group largely affect the relaxation dynamics. In this occasion, it enhanced the dielectric strength. The local backbone motion (local segmental motion), named as β-relaxation was observed both in dried and wet states. The relaxation strength decreases after drying the sample. This may be due to the ability of water to act as plasticizer. Water molecules expand the space between the chain molecules decreasing the sterical hindrance for the local chain motion and open the fixing hydrogen bonds and the water dipoles adsorbed increase the effective dipolar moment of the polar sites. The activation energy of β-process increased by adding water molecules in small amounts. The activation energy of β-process were 41.34 and 61.38 kJ/mol for dried and wet samples, respectively. The β-relaxation disappeared in wet samples at higher temperatures, it was simply because of the existence of a strong β_{wet}-relaxation in higher temperatures region that makes unable to resolute β-relaxation in that region. The pre-exponential factor τ_0 is 3.58701×10^{-10} and 6.67474×10^{-15} s for dried and wet samples, respectively.

The temperature variation of relaxation time ($\tau_{\beta\text{-wet}}$) of β_{wet}-relaxation (Fig. 6a) observed in wet samples indicates that a transition occurs at 30 °C ($3.3k/T$). This variation with temperature obeys Arrhenius law (straight line behavior) on both sides of transition point except very near to the transition point where the molecules in the system became unstable or free of rotational constraint. Majumder, Mitra, and Roy (1994) and Majumder, Roy, and Roy (1996) observed the similar behavior of relaxation phenomena, which corresponds to liquid crystalline phase transition. In this case, the variation of relaxation time (Fig. 6a) and dielectric strength (Fig. 6b) of β_{wet}- with temperature on both sides of transition indicate a transition could occur. So, the β_{wet}-relaxation in wet sample is nothing but a soft mode relaxation those arose due to a collective motion of water–polymer matrix in combined. Colonna, Buleon, and Mercier (1987) indicates that an inter-crystalline phase transitions can occur at low water contents. Based on that reason, we can expect an inter-crystalline phase transition occuring at ca. 30 °C in wet wheat starch samples studied.

4. Conclusion

Three distinct β-, δ- and β_{wet}-relaxations were found in wet sample while four distinct σ-, δ-, β- and γ-relaxations were found in dried sample. The activation energy associated with β-relaxation was increased in wet sample in comparison with dried sample and the pre-exponential factor τ_0 of the relaxation times was decreased. It simply indicates that the entropy of segmental motion of the polymer chain was increased in wet sample influenced by a strong hydrogen bond with AGUs.

The β_{wet}-relaxation only observed in wet sample associated with a collective motion of a water–polymer-mixing phase may have a clear relation with intermediate phase transition. Such relaxation indicates that a phase transition occurs at ca. 30 °C. It resembles with the soft mode (Majumder, Mitra, & Roy, 1994; Majumder, Roy, & Roy, 1996) in liquid crystals, although we are not ascertain about the characteristics and behavior of such transition in this case. It is more likely an inter-crystalline transition (Colonna, Buleon, & Mercier, 1987). It is a most interesting fact that the δ-relaxation disappeared at low temperature in wet sample while it was observed in dried sample with non-Arrhenius behavior. The δ-relaxation was observed only in dried sample due to the movement of ions that arose due to water and AGUs interaction at the surface of electrode only at very low water content in the sample (<2–3%) shows an Arrhenius behavior.

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