

## Enhanced Electrochemomechanical Behaviors of Polyaniline Films by Chloride Concentrations

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Electrochemomechanical deformations (ECMD) of polyaniline film have been enhanced in hydrochloric acid (HCl) equilibrated in pH 1.2 with sodium chloride (NaCl). The maximum film deformation has been reached to 7%, which is two times larger than that observed in 1 M HCl. Taking the pH dependence of redox-potential into account, this enhancement can be explained by the increase of anion doping ratio.

Several attractive results have been reported in the electrochemical actuator using conducting polymers.<sup>1–3</sup> In those reports, the several novel materials and organic additives have been proposed for achieving the excellent performances of electrochemomechanical deformations (ECMD).<sup>1–4</sup> In the viewpoints of substantial applications, however, the actuation in aqueous media is still one of the important requirements for practical executions. In the case for the ECMD evaluation, several environmental conditions, such as pH, electrolyte concentration and temperature, are supposed to affect the deformation performances.

Among the conducting polymers, polyaniline (PAni) has been regarded as one of the feasible materials because of solution processability, synthetic versatility and reversibility in redox reactions.<sup>5</sup> However, the requirement of low pH for conserving the redox activities and the small deformations of 4% in HPF<sub>6</sub><sup>2–4,6</sup> offer a stumbling block towards their biomedical applications. The efforts to elevate the active pH regions and ECMD magnitudes are important challenging tasks for PAni actuator.

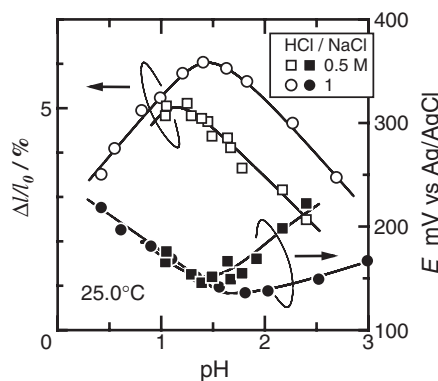
This work presents our recent results pertaining to the attainment of large expansion in the PAni film by subtle selection of environmental conditions during electrochemical process. The maximal ECMD magnitudes were found to be around 6–7% in HCl/NaCl solutions, around two times larger than that reported earlier.<sup>6,7</sup>

ECMD were measured by means of the direct measurement system reported earlier.<sup>5,8</sup> In this study, a jacket-built-in glass cell was employed for stabilizing the temperature by a circulating controller (Julabo F25-MP). Temperature was calibrated by plotting the relationships between the sample and the control temperatures. PAni films were cast from 3 wt % *N*-methyl-2-pyrrolidone solutions followed by the protonation in 1 M HCl by sonication. A strip with 5 mm in length, 1.7 mm in width, and 15  $\mu$ m in thickness was used as the sample of emeraldine from the initial state. pH was adjusted to a defined value by mixing different volume of HCl and NaCl electrolytes having the same Cl<sup>–</sup> concentrations. Ag/AgCl and Pt were used as the reference and the counter electrodes, respectively. KEYENCE LB-1000/LB-040 laser displacement meter was employed for obtaining

the film deformations. Cyclic voltammetry (CV) was performed from leucoemeraldine to emeraldine salt state in the range of –200 to 550 mV vs Ag/AgCl swept with 2 mV/s.

Independent from pH and electrolyte concentrations, all ECMD behaviors exhibited the maximum and the minimum at oxidation and reduction potentials, respectively.<sup>5–7</sup> In the case of the ECMD magnitude ( $\Delta l/l_0$ ), it markedly increased to 6% from pH 0.5 to 1.5 and then turned to decrease as a function of pH over 1.5 in 1 M HCl/NaCl solutions (Figure 1). It should be noted that the electrolytes were prepared by biological electrolytes such as HCl and NaCl in contrast to the synthesized ions such as PF<sub>6</sub><sup>–</sup>. The anion concentration is fixed throughout the measurements. Therefore, the variation of ECMD magnitudes described above should be due to the change of pH, viz., the cation concentrations. In the case for the solutions prepared with 0.5 M HCl and 0.5 M NaCl, the maximum of ECMD magnitude was relatively small but still 5% at pH 1.5 followed to the decrease of deformation magnitudes.<sup>6</sup> This indicates that the anion concentration plays a dominant role for exhibiting the enhancement of ECMD behaviors in PAni film.

The redox potential was found to decrease with increasing pH from 0.5 to 1.5 in 1 M HCl/NaCl solutions. At higher pH, the redox potentials turned to increase (Figure 1). According to the Nernst equation, the potential slope represents the polarity of transported ions in the redox reactions.<sup>8,9,11</sup> This indicates that at low pH region (pH < 1.5), proton is the major mobile ion (negative slope against pH) and therefore, the low pH region can be expressed as the proton-controlled region. In the case of potential dependence in higher pH region, the obtained positive slope rules out this possibility, thus it can be expressed as the non-proton-controlled region.

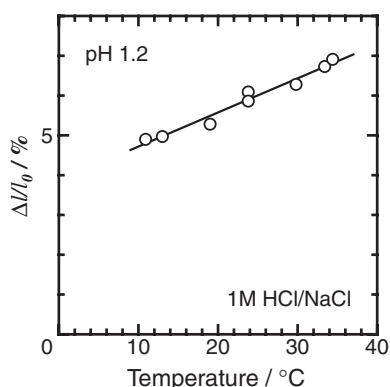


**Figure 1.** pH dependences of ECMD magnitudes ( $\Delta l/l_0$ , in which  $\Delta l$  and  $l_0$  represent the change in length and the original length of PAni film of emeraldine salt state, respectively) and half redox potentials ( $E$ ) in 1 M and 0.5 M HCl/NaCl electrolytes.

The cation injection tends to show the cathodic expansions in the ECMD characteristics,<sup>12</sup> suggesting that the decreased magnitudes at lower pH could be explained as the result of counteractions of the relatively large anodic expansions and the coexisting small cathodic expansions. In this case, the anodic expansions can be associated with the persistent anion injection, the conformational changes of main-chain or the change of electrostatic repulsive forces due to the polycation formation in PANi.<sup>6</sup> The increase of pH, however, weakens the proton contribution into the redox reactions following the decrease in the cathodic expansions. Therefore, the anion contributions alternatively become dominant, resulting into the enhancement of anodic expansions.

In the diluted electrolytes having concentration up to 0.5 M, ECMD magnitudes were found to reduce at all the pH regions (viz., from pH 0.5 to 3.0) with the maximum ECMD magnitude still up to 5%. Especially, in the pH region having the positive slope of redox potential, the large difference of ECMD magnitudes with the change of anion concentrations indicates that this can be expressed as the pH region having the strong dependence on the anion concentration. As one possible explanation, the decrease of ECMD magnitudes in this pH region, therefore, can be explained with the decrease of the anion insertions. The decrease of ionic conductivity of electrolyte and the decrease of electron conductivity in PANi film with dilution of proton<sup>13,14</sup> also might be the other reasons. In any case, the pH dependence of half redox-potential changed from the negative slope to the relatively positive slope around at the same pH regions showing the maximum ECMD behaviors. This indicates that the comprehensive characteristics of ECMD behaviors and redox-potential shifts were essentially conserved in the change of electrolyte concentrations.

It was found that the collected charges during redox reactions were constant at pH < 1.5. The drastic increase of ECMD behavior at pH < 1.5, therefore, can be attributed to the decrease of the cathodic expansive portion by proton insertion and the coincident increase of anodic expansive portion by Cl<sup>-</sup> insertion with pH elevation. Over increasing the pH greater than 1.5, the redox charge turned to decrease as a function of pH, which can be associated to the depression of electrochemical activity in PANi. The efficiency of ECMD behavior ( $\eta$ ) can be represented as the magnitude of ECMD per unit-injected charges.<sup>13,15</sup> The enhancement of ECMD magnitude in Figure 1, therefore, raises



**Figure 2.** Temperature dependence of ECMD magnitudes ( $\Delta l/l_0$ ) in 1 M HCl/NaCl electrolyte.

$\eta$  in pH < 1.5. It can be explained by the hindrance of proton insertion, viz., the decrease of potentially existing cathodic expansions. The redox charges, therefore, contribute to the anodic expansions effectively.

Figure 2 shows the temperature dependence of ECMD magnitude at the constant pH of 1.2. The ECMD magnitude was found to increase linearly from 10 to 40 °C. Kato et al.<sup>16</sup> have also reported the effect of temperature on the performance of electrochemical actuator. In this case, the bending speed was extremely increased with increasing temperatures. These results indicate that the elevation of temperature essentially enhances the ECMD performances in terms of the speed and the deformation magnitudes coincidentally. The linear dependence of ECMD magnitude provides a method to evaluate the thermal expansion coefficient of the PANi freestanding film. It was estimated to be about 0.086%/K as electrochemomechanical mode, indicating that the 10 °C elevation increases the ECMD magnitude by about 0.9%.

In conclusion, the optimization of pH and electrolyte concentration with temperature ensures the enhancement of ECMD behaviors. It was found that the environmental tunings have a good impact on the ECMD performance of PANi soft actuator. The magnitudes of ECMD have been found to increase from 3.5% at pH 0.4 and 25 °C to 7.0% at pH 1.2 and 34 °C in the polyaniline film. This enhancement was achieved in the conventional electrolytes mixed with HCl and NaCl solutions. The results indicate that the other actuator systems such as polypyrrole also have the possibility of ECMD enhancement by the environmental optimizations.

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