

Strain and Energy Efficiency of Polyaniline Fiber Electrochemical Actuators in Aqueous Electrolytes

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The electrochemical linear actuation of polyaniline fiber actuators has been studied in a variety of acidic aqueous electrolytes. Experimental results show that the linear strain changes significantly but nonlinearly with the anion volume. For anions smaller than Br^- , a larger strain was obtained for a larger anion, that is, $\text{Br}^- > \text{Cl}^- > \text{F}^-$, while once the anion was larger than Br^- , a larger anion produced a smaller strain, that is, $\text{BF}_4^- > \text{ClO}_4^- > \text{CF}_3\text{SO}_3^-$. On the basis of the definition of the ECR (elongation/charge ratio), that is, the contribution of a unit charge to fiber elongation, the maximum linear strain can be estimated by assuming the electrochemical efficiency is 100%. Furthermore, under isotonic conditions and the application of a constant voltage, the energy efficiency without energy recovery was shown to be proportional to the ECR and applied force and inversely proportional to the applied voltage. Under the same conditions, the highest energy efficiency is obtained in HBr. By assuming that ion and solvent insertion contributes mostly to the fiber expansion, a simple mathematical description is developed for the linear strain to show how it is determined by the volume and carried charge of the insert complex and the anisotropy of the fiber. The difference between the theoretical and experimental results suggests that due to the crystallite structure, not all exchanged charge contributes to the fiber expansion. As the anion becomes larger, it may become more difficult for the anions to be inserted into the polymer fiber.

1. Introduction

Conducting polymers have been explored as novel electrochemical actuators, largely owing to their unique properties of light weight, high stress generation, and low operational voltages. Dimensional changes of conducting polymer electrochemical actuators have been attributed in varying degrees to counterion transport into/out of the polymer, solvent molecule transport into/out of the polymer, morphological change of the polymer, and electrostatic expulsion between polymer chains.¹ In terms of the conversion of the electrical energy into the mechanical work of a conducting polymer electrochemical actuator upon an electrochemical event, significant research^{2–7} has demonstrated that the linear strain of the actuator is proportional to the redox charge of the electrochemical reaction of the polymer. Additionally, Kaneko et al. studied the effect of electrolyte anion size on the linear strain of polyaniline films⁸ and observed that the linear strain slightly depended on the volume of anions. Herod et al.³ studied the linear strain of polyaniline films in the protonic acid doping process (no potential is applied) in different acids and noticed that the doping time rather than the anion size determines the elongation. However, a detailed study that focused on how the linear dimensional change of a conducting polymer electrochemical actuator is determined by the properties of the polymer and the electrolyte has not yet been reported.

In this paper, we studied the electrochemical linear actuation of polyaniline fiber actuators in a variety of aqueous acidic electrolytes and subsequently discussed the maximum linear strain and energy efficiency of the actuator. Finally, assuming ion insertion contributes mostly to the fiber expansion, we

developed a simple mathematical description of how the linear strain of the actuator is dependent on the volume and carried charge of the inserted anion, the dimensions (radius and length) of the fiber, and the anisotropic factor of the fiber.

2. Experimental Section

2.1. Chemicals and Materials. All reagents were analytical grade. Aqueous acid solutions were prepared at a concentration of 1.0 M by diluting the concentrated acids with deionized water.

The polyaniline fibers used in this study were prepared using a slightly modified procedure published by Pomfret et al.⁹ In general, 4.22 g of high molecular weight emeraldine base and 5.78 g of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMP-SA) were ground together for five minutes with a mortar and pestle. The gray powder was then placed inside a glovebag together with 190 g of dichloroacetic acid (DCAA), and the bag was filled with nitrogen gas. The powder was added gradually to the DCAA solvent and homogenized. The thick solution was then sealed and transferred to a fiber spin line. A nitrogen pressure of 100 psi was applied to one end of the dope pot. The other end of the dope pot was attached to a gear pump. The spin solution was passed through 240 and 140 μm filters before being extruded through a 250 μm diameter spinneret into a 2-butanone coagulation bath. The nascent fiber was removed after 10 min and allowed to dry overnight. The polyaniline fibers were then stretched approximately 200% by slowly passing the fiber over a 90 °C heat source (a soldering iron whose tip was wrapped with a thin PTFE film). This has the effect of aligning the polymer chains approximately parallel to the stretch direction, thereby increasing the tensile strength, Young's modulus, and electrical conductivity of the polyaniline fiber along its alignment axis. The stretched fibers had a diameter of $\sim 90 \mu\text{m}$ and an electrical conductivity of $\sim 1000 \text{ S/cm}$.

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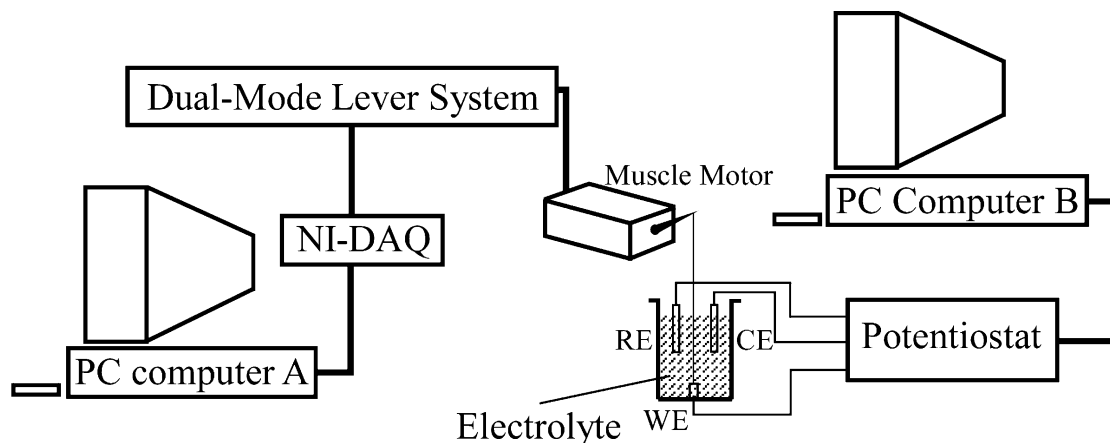


Figure 1. Diagram of the experimental apparatus used for electrochemical actuation measurements of polyaniline fibers.

2.2. Experimental Apparatus and Measurements. Electrochemical actuation measurements of polyaniline fiber electrochemical actuators were performed using the apparatus shown in Figure 1. A three-electrode electrochemical cell was used, which consisted of the polyaniline fiber as the working electrode, a Ag/AgCl reference electrode, and a Pt wire counter electrode. One end of the fiber was clamped to the bottom of the electrochemical cell and electrically connected with a platinum plate. This contact was connected to the working electrode of an EcoChemie pstat30 potentiostat. The other end of the fiber was fixed using an epoxy resin onto the tip of the arm of a lever arm system (Aurora Scientific, model 300B). Computer A controlled the muscle lever system and acquired the actuation signal of the fiber through a NI-DAQ system (National Instruments), which consisted of a PCI-6052E DAQ coupled with a BNC-2090 BNC adaptor. Computer B controlled the electrochemical stimulation applied on the fiber through the potentiostat. A trigger line synchronized the programs in computer A and computer B so that the electrochemical stimulation and the fiber actuation were recorded simultaneously.

3. Results and Discussion

3.1. Strain in Different Acid Electrolytes. In order to obtain well-defined electroactivity for the polyaniline fibers, we performed the measurements in acidic electrolytes at a relatively high acid concentration of 1.0 M.¹⁰ Also, to avoid polyaniline degradation,¹¹ the potential range was limited to -0.2 to 0.6 V so that potential was only cycled over the first redox process of polyaniline, that is, leucoemeraldine \rightleftharpoons emeraldine. In this potential range, stable cyclic voltammograms (CVs) and actuation were obtained for the polyaniline fibers after potential cycling for 20 cycles. CVs of a polyaniline fiber obtained in different acids are shown in Figure 2. Although a typical CV of polyaniline was observed in all acids, the CV shapes and peak positions varied significantly in these acids. On the basis of the anion exchange behavior of polyaniline in the potential range used,¹⁰ its electrochemical behavior would be affected by the properties of the anions in the electrolyte. We found that the difference in anion size of these acids was responsible for this observation. Except for F^- , the oxidation peak shifted anodically and became wider as the anion size increased (Figure 2, Table 1). This indicates that anion insertion into the polyaniline fiber for charge compensation becomes more difficult for larger ones. Nevertheless, despite the smallest size of F^- , the polyaniline fiber showed a high oxidation peak potential in HF. Most likely, this is associated with the large solvation sphere and the poor dissociation of HF ($pK_a = 3.20$)

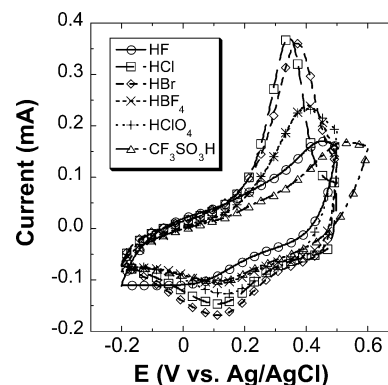


Figure 2. Cyclic voltammograms of a polyaniline fiber obtained in different acids. Concentration of acid: 1.0 M. Diameter of fiber: 89 μm . Effective length of fiber: 11 mm. Scan rate: 5 mV/s. Applied load: 1 g.

TABLE 1: Effect of Anion Sizes of Different Acids on Oxidation Peak Potential (E_{pa}) and Strain of a Polyaniline Fiber

anion	volume (\AA^3) ^a	E_{pa} (V)	strain (%)
F^-	10.3	0.45	0.76
Cl^-	24.4	0.34	1.05
Br^-	31.0	0.37	1.18
BF_4^-	41.6	0.40	0.57
ClO_4^-	52.9	0.40	0.51
$CF_3SO_3^-$	70.4	0.53	0.40

^a Volumes of F^- , Cl^- , and Br^- are van der Waals volumes.¹² Volumes of BF_4^- , ClO_4^- , and $CF_3SO_3^-$ were calculated using HyperChem, release 7.

in aqueous electrolyte compared with all other acids used, which have pK_a 's less than 1. It has previously been shown that the electroactivity of polyaniline is strongly dependent on the acidity of the electrolyte.¹⁰

In terms of electrochemical actuation, the actuation profiles of extension upon oxidation and contraction upon reduction were obtained for the polyaniline fiber in all acids (Figure 3). The actuation profiles are similar to previously reported results⁸ and indicate typical anion exchange behavior of polyaniline in the potential range used. Furthermore, the linear strains obtained from the responses to the SWP (square wave potential) of 500 s (Figure 4, parts a and b) in HCl, HBF₄, and CF₃SO₃H are almost the same as that in Figure 3, showing that the linear strains obtained in Figure 3 are not kinetically affected. However, the magnitude of the linear strain was found to be dependent on the electrolytes. This can again be associated with anion sizes in the electrolyte. As summarized in Table 1, for

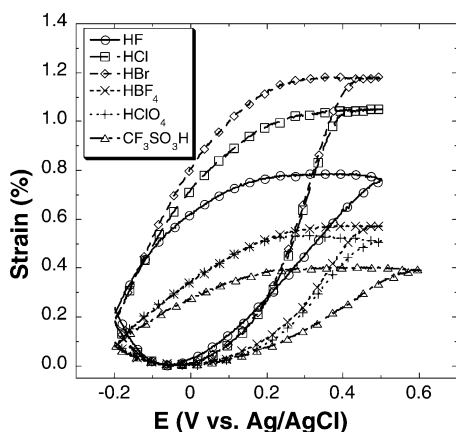


Figure 3. Corresponding linear strain of the same polyaniline fiber used in Figure 2.

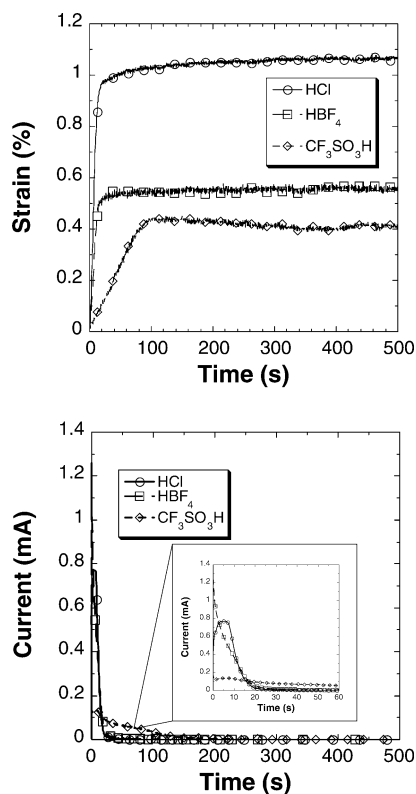


Figure 4. (a) SWP (square wave potential)-induced isotonic linear strains in HCl, HBF₄, and CF₃SO₃H. SWP: -0.2V to 0.4 V, 500 s. Applied load: 1 g. (b) Corresponding current responses to the SWP in (a).

anions smaller than Br⁻, a larger strain was obtained for a larger anion, that is, Br⁻ > Cl⁻ > F⁻. In contrast, once the anion was larger than Br⁻, a larger anion produced a smaller strain, that is, BF₄⁻ > ClO₄⁻ > CF₃SO₃⁻. To further understand this phenomenon, we tried to correlate fiber actuation with the charge that could be passed through the fiber in different acids.

By integrating the current passed through the fiber upon potential cycling, we were able to investigate the relationship between the electrochemical actuation and the charge that was injected and removed during the redox cycle. For example, Figure 5 shows that the fiber extended and contracted in the HCl electrolyte, which accompanied, respectively, the injection and removal of the charge. (The curves in other acids are similar to that in HCl.) Indeed, it has been stated that, in a conducting polymer system, the volume change of the polymer is caused by the charge exchanged with the electrolyte.^{1,6} For a conducting

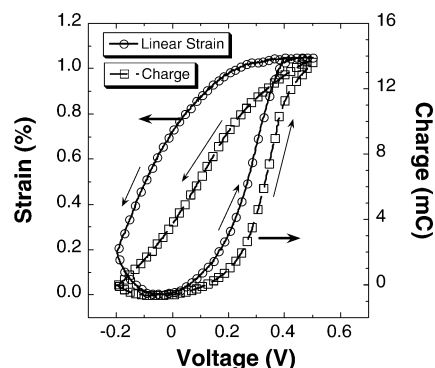


Figure 5. Linear strain and faradaic charge of a polyaniline fiber as a function of scanning potential in 1.0 M HCl. Other conditions as in Figure 2.

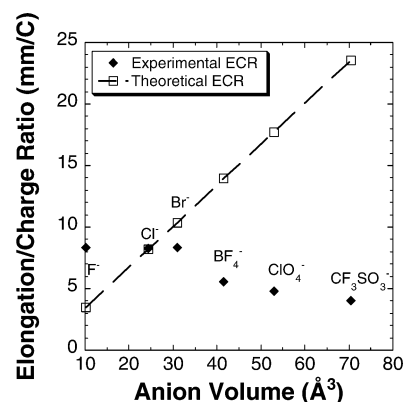


Figure 6. Comparison between the theoretical and experimental elongation/charge ratio (ECR) for different anions. The charge used for the calculation of the ECR was obtained by integrating the CV currents obtained in Figure 2.

polymer electrochemical actuator under equilibrium conditions, the actuation is proportional to the exchanged charge.⁶ Furthermore, to investigate the effect of charge on the fiber actuation in different acids, we divided the fiber elongation by the charge obtained in different acids, resulting in an elongation/charge ratio (ECR). More specifically, the ECR represents a proportionality coefficient of the linear relationship between the strain and the charge, that is, the contribution of a unit charge to the fiber elongation. It is interesting to notice that the value of the ECR varies with different anions (Figure 6, experimental ECR). Similar ECR values were obtained for F⁻ and Cl⁻, but a slightly higher ECR value was observed for Br⁻. However, for anions larger than Br⁻, the ECR consistently decreased as the anion size increased. This fact implies that properties of anions play an important role in determining the polyaniline fiber actuation.

3.2. Electrochemical Efficiency and Maximum Strain Estimation. On the basis of the ECR values, we can also estimate the maximum theoretical strain for the polyaniline fiber actuator. Considering the varied electroactivity of a conducting polymer under actual experimental conditions, we define an electrochemical efficiency, ζ , as the ratio of the charge observed during the redox process to the total charge theoretically expected in the polymer. Assuming $\zeta = 100\%$, with the ECR values, we can estimate the maximum strain of the polyaniline fiber actuator in a specific electrolyte. For a polyaniline fiber (radius, r ; length, h) the theoretically expected charge Q can be calculated as

$$Q = \frac{F\rho n\pi r^2 h}{M_w}$$

and thus the maximum strain ϵ_{\max} as

$$\epsilon_{\max} = \frac{Q(\text{ECR})}{h} = \frac{F\rho n\pi r^2(\text{ECR})}{M_w} \quad (1)$$

where F is the Faraday constant, ρ is the density of the polymer fiber, n is the number of electrons transferred in the redox process of the polymer for every repeating unit, and M_w is molecular weight of the polymer repeat unit. For polyaniline, every tetramer repeat unit involves a two-electron transfer for the first redox process of leucoemeraldine \rightleftharpoons emeraldine, and therefore, the theoretical values of n and M_w are 2 and 362.4 g/mol (emeraldine base), respectively.

Using HCl as an example, the maximum strain that can be expected for the polyaniline fiber used in this work ($r = 89 \mu\text{m}$, $\rho = 1.44 \text{ g/cm}^3$ for the emeraldine base form) is $\epsilon_{\max} = 3.9\%$ according to eq 1. However, the actual strain of the fiber obtained in HCl was only 1.1% (see Table 1). The wide discrepancy between these values should be associated with the low electroactivity of the fiber. Indeed, we have observed low electrochemical efficiencies for the polyaniline fibers used in this work (e.g., 26% in HCl). To improve the electrochemical efficiency and electrochemical actuation for polyaniline fibers, we are currently pursuing a next generation of fiber that possesses smaller diameters and higher conductivity.

3.3. Energy Efficiency. Upon actuation through the conversion of the input electrical energy into mechanical work of an electrochemical actuator, if the reusable energy is excluded (the worst case), the energy conversion efficiency \hat{e} can be expressed as

$$\hat{e} = \frac{\int f dx}{\int V(t)I(t) dt} \quad (2)$$

where f is the force applied on the actuator, x is the fiber elongation in the force direction, $V(t)$ is the applied voltage, and $I(t)$ is the current. Under isotonic conditions, f is the constant applied force f_a , and Δh is the linear elongation. Accordingly, eq 2 can be changed to

$$\hat{e} = \frac{f_a \Delta h}{\int V(t)I(t) dt} \quad (3)$$

During practical operation of these actuators, a constant voltage V (between the oxidation and the reduction potentials) is typically employed. Thus, the efficiency \hat{e} can be simplified to

$$\hat{e} = \frac{f_a \Delta h}{V \int I(t) dt} = \frac{f_a \Delta h}{VQ} = \frac{f_a}{V}(\text{ECR}) \quad (4)$$

Equation 4 indicates that the energy efficiency of a polyaniline fiber electrochemical actuator is determined by the operation conditions of the actuator, properties of the fiber material, and properties of the electrolyte. During the operation of the actuator, the applied force f_a and the applied voltage V are two important parameters. Increasing the applied force f_a would enhance the energy efficiency. However, the applied force is limited by the mechanical properties of the fiber, for example, modulus, strength, and elasticity. Too much force could cause creeping actuation, irreversible actuation, and even breakage of the fiber. Voltage V inversely affects the energy efficiency. Application of a small V will increase the energy efficiency but unfortunately

decrease the linear extension due to the incomplete oxidation of the fiber. Improving the electroactivity of the fiber (e.g., increasing the conductivity of the fiber by the use of a high molecular weight polymer and the stretching of the fiber) would enable the redox process of the fiber to occur at lower potential which should eliminate this problem. In terms of the electrolyte, the properties of the anions are an important factor. The ECR value is inherent for a given electrolyte and the polymer fiber. Among all the acids used in this paper, Br^- has the highest ECR value and thus the highest energy efficiency according to eq 4. In a typical operation test, a constant voltage of 0.6 V and a stress of 2 MPa (1.3 g) were applied to the fiber actuator. This corresponds to a maximum energy efficiency of 0.017% in HBr.

3.4. Further Discussion. In a conducting polymer electrochemical system, ion and solvent insertion for charge compensation contributes substantially toward the volume change of the polymer.^{1,13} Ideally, for a dense fiber (i.e., no free volume within the fiber) in an electrolyte under constant temperature and air pressure, its total volume, upon the insertion of N rigid particles with the volume of v for each particle, can be expressed as

$$Nv + \pi r^2 h \quad (5)$$

where r and h are the radius and length of the fiber, respectively.

Compared to the dimension of the conducting polymer fiber, the size of the inserted species is extremely small. Assuming that these particles uniformly distribute within the fiber, and based on our experimental result that effect of the external load on fiber actuation is negligible at the normally used load (less than 1.5 g or 2.3 MPa), the length extension Δh and radius extension Δr of the fiber are proportional to its length h and radius r . Therefore,

$$\frac{\Delta r}{r} = k \frac{\Delta h}{h} \quad (6)$$

where the real number k is induced by the anisotropic nature of the polymer.

According to eq 5, the increase in the volume of the fiber is given by

$$\Delta V = \pi(r + \Delta r)^2(h + \Delta h) - \pi r^2 h = \pi r^2 h \eta_d v \quad (7)$$

where

$$\eta_d = \frac{N}{\pi r^2 h} \quad (8)$$

Combining eqs 6 and 7 results in

$$\left(1 + k \frac{\Delta h}{h}\right)^2 \left(1 + \frac{\Delta h}{h}\right) = 1 + \eta_d v \quad (9)$$

In all experimental results, the linear strain $\Delta h/h$ is less than 2.0%. For polyaniline films developed in NMP (*n*-methyl-2-pyrrolidinone) solution, it has been reported in Herod et al.'s work³ that the expansion coefficient ratio between the perpendicular and parallel directions is about 3.8. However, in ref 3, expansions in parallel and perpendicular directions were measured independently, and the creep in the perpendicular direction shows that there was too much tension applied on the film and the film morphology was changing when the strain was measured. For the polyaniline thin fibers described in this paper,

with the use of an Olympus DP11 digital camera connected to a Navitar microscope, the average strain value of 1.2% in 10 cycles was obtained in HCl for the fiber diameter expansion. Compared to the linear fiber strain of 1.1% in HCl, k is about 1.1. Mathematically, if $k < 3.0$, eq 9 can be approximated to within 5% error as

$$\frac{\Delta h}{h} \approx \frac{1}{2k+1} \eta_d v = \frac{1}{(2k+1)} \frac{N}{\pi r^2 h} v \quad (10)$$

Under equilibrium conditions, charge compensation is usually achieved by the insertion of counterions from the electrolyte into the conducting polymer.^{1,6} Consequently, the number of inserted counterions, N , can be expressed as

$$N = \frac{Q}{N_e e} \quad (11)$$

where Q is the total charge exchange upon redox process of the polymer, N_e is charge number of the counterion, and e is the charge of an electron.

Compared with the volume of the inserted ions, the volume of the carried electrons and protons is much smaller and could be negligible. Thus, the volume v in eq 10 is still the volume of the inserted species, which can be either ion alone or ion together with its carried solvent molecules in some cases. Therefore, upon combining eqs 10 and 11, the linear strain, ϵ , for a conducting polymer fiber during its electrochemical actuation can be described as the following equation:

$$\epsilon = \frac{\Delta h}{h} \approx \frac{1}{2k+1} \eta_d v = \frac{1}{(2k+1)} \frac{Qv}{\pi r^2 h N_e e} \quad (12)$$

According to the eq 12, the ECR is

$$\text{ECR} = \frac{\Delta h}{Q} = \frac{1}{(2k+1)} \frac{v}{\pi r^2 N_e e} \quad (13)$$

Note that the value of ECR changes with the fiber diameter. To use the ECR value described in this paper for fibers with different diameters, the ratio of strain to charge density, $\epsilon \pi r^2 h / Q$, should be calculated based on eq 13:

$$\frac{\epsilon \pi r^2 h}{Q} = \pi r^2 (\text{ECR}) = \frac{1}{(2k+1)} \frac{v}{N_e e} \quad (14)$$

The ratio of strain to charge density is only determined by the electrolyte and material, that is, the volume of the inserted ion v , the charge number of the counterion N_e , and the anisotropic factor k .

Since the ECR is the contribution of a unit charge to the fiber elongation, according to eq 12, ECR is proportional to the volume of the inserted ion. With the use of the volumes of the different anions listed in Table 1 and the assumption $k = 1$, theoretical ECRs were calculated and are shown in Figure 6. Assuming that these anions can freely be inserted/deinserted into/out of the polymer upon redox cycling, an enhanced strain would be expected for a larger anion. However, the experimental data shown in Figure 6 does not support this hypothesis. When the values obtained experimentally and theoretically for the ECR are compared, it is possible to explain the actuation mechanism of the polyaniline fiber in different acids.

As shown in Figure 6, the experimental result for Cl^- fits perfectly with its theoretical expectation, which indicates that Cl^- can freely transport into and out of the polymer during redox cycling in HCl. However, for anions smaller or larger than Cl^- , different insertion types of anions would be possible. For F^- , which is smaller than Cl^- , its experimental ECR is larger than the theoretical prediction: according to the experimental ECR, the effective volume of a complex calculated from eq 13 is 24.9 \AA^3 , which is larger than the volume of one F^- (10.3 \AA^3). However, the volume of 24.9 \AA^3 is just the combination of one F^- (10.3 \AA^3) and one water molecule (14.6 \AA^3). This fact suggests that, during the redox process of the polyaniline fiber in HF, the inserted species are F^- and water molecules in the ratio of 1:1 (one F^- with one water molecule). For anions larger than Cl^- , their experimental ECRs are smaller than the theoretical ones, and the difference in ECR between the experimental and the theoretical becomes larger when the volume of the anion increases, that is, $\text{CF}_3\text{SO}_3^- > \text{ClO}_4^- > \text{BF}_4^- > \text{Br}^-$. This suggests that these anions cannot completely diffuse into the polymer for charge compensation. In fact, the crystalline structure of the polymer has been shown to introduce an additional resistance for ion insertion.^{14,15} This resistance would be higher for larger-size ions. If some of the anions required to compensate the polymer's redox charge are not inserted into the fiber, then the charge Q in eq 12 will be only a part of the total charge exchange. The effective charge that contributes to the fiber expansion can be calculated by using eq 12.

3.5. Effects of the Applied Force. As stated earlier during the construction of the model in section 3.4., load-induced dimensional change of the fiber was neglected, resulting in eq 12. According to Spinks et al.,¹⁶ this is valid when a small isotonic force is applied. In fact, when an isotonic force less than 1.5 g (2.3 MPa) was applied to the polyaniline fiber, the effect of load on fiber strain in the potential range used was negligible. However, at a higher load, the effect of load should be taken into account. Referring to Spinks et al.,¹⁶ eq 12 can be modified to

$$\begin{aligned} \epsilon &= \frac{1}{(2k+1)} \frac{Qv}{\pi r^2 h N_e e} + \\ &\quad f_a h [\pi^{-1} (r + \Delta r)^{-2} Y_o^{-1} - (\pi r^2 Y_r)^{-1}] \\ &\approx \frac{1}{(2k+1)} \frac{Qv}{\pi r^2 h N_e e} + \frac{f_a h}{\pi r^2} (Y_o^{-1} - Y_r^{-1}) \end{aligned} \quad (15)$$

where Y_o and Y_r are the Young's Modulus of the fiber in the oxidation and reduction states, respectively. In eq 15, the second term represents the effect of the applied load on the strain of fiber. The difference in the Young's Modulus between the oxidation and reduction states determines how strongly the load affects the strain.

4. Conclusions

The electrochemical linear actuation of polyaniline fiber actuators in a variety of acidic aqueous electrolytes was studied. The linear strain is not proportional to the anion volume. For anions smaller than Br^- , a larger strain was obtained for a larger anion, that is, $\text{Br}^- > \text{Cl}^- > \text{F}^-$. In contrast, once the anion was larger than Br^- , a larger anion produced a smaller strain, that is, $\text{BF}_4^- > \text{ClO}_4^- > \text{CF}_3\text{SO}_3^-$. On the basis of the definition of the ECR (elongation/charge ratio), the contribution of a unit charge to fiber elongation was studied, and the maximum linear

strain can be estimated by assuming the electrochemical efficiency is 100%. Furthermore, in the worst case, if no energy can be reused, the energy efficiency under isotonic conditions when a constant voltage is applied is proportional to the ECR and applied force and inversely proportional to the applied voltage. Under the same conditions, the maximum energy efficiency will be obtained in HBr. By assuming that ion and solvent insertion contributes mostly to the fiber expansion, a mathematical description is developed for the linear strain. If the linear strain is less than 2.0%, and the anisotropic factor, k , which is defined as the ratio between the strain in the perpendicular and parallel directions, is less than 3.0, then the linear strain is approximately proportional to the exchanged charge density and volume of the insert ion and inversely proportional to the charge number of the insert complex. The mathematical description is perfect for Cl^- . And the difference between the experimental results and that calculated from the mathematical description suggests that, in HF, the inserted species are F^- and water molecules in the ratio of 1:1. Anions larger than Cl^- produce a smaller ECR than that estimated from the equation. The difference suggests that due to the crystallite structure, not all exchanged charge contributes to the fiber expansion. As the anion becomes larger, it becomes difficult for the anions to be inserted into the polymer fiber.

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