Influences of Co-monomers and Electrolyte Acidity on Morphological Structure of Copper-in-Copolymer Gradient Film

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ABSTRACT: In this paper, the influences of composition of copolymers and acidity of electrolyte in an electrochemical reactor on morphological structure of copper-in-polymer gradient composite film were investigated. For binary copolymers, poly(acrylonitrile-*co*-methyl acrylate) [P(AN-*co*-MA)] and poly(acrylonitrile-*co*-sodium allyl sulfonate) [P(AN-*co*-SAS)], the charged group $-SO_3^-$ in P(AN-*co*-SAS) improves the swelling of the copolymer phase and copper reduction to form gradient morphology; the carboxylic ester group in P(AN-*co*-MA) is not effective because of its poor hydrophilicity, but it is a cooperating component with P(AN-*co*-SAS) to avoid excess of counterion (i.e., Na^+) in SCF, which might severely interrupt Cu^{2+} coexistence. The swelling of the polymer phase is helpful to decrease the energy of the transfer ions in SCF and to enhance copper deposition and gradient formation. The increase of surface energy because of cluster growth raises the surface energy level of deposited Cu^0 clusters. The conteraction between these two energy factors allows the size of clusters to be 50–100 nm. The appropriate H^+ concentration improves active Cu^{2+} reduction and thus deposited gradient copper phase in the copolymer matrix.© 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 373–380, 2004

Key words: polyacrylonitrile; copper; gradient composite; electrochemical; methyl acrylate; sodium allyl sulfonate

INTRODUCTION

Gradient composites are considered to be the materials in which the concentrations of two different components change gradually over their cross section. The properties and functions within those materials correspond to the position in the cross section. The gradient morphology in those materials is ideal to resolve various kinds of interface problems.[1,2] There has been research in this field focused on metal–ceramic or metal–metal gradient materials.[3–6] Functionally gradient metal-matrix composites (F-G MMC) offer the advantage of continuously varying mechanical and thermophysical properties such as strength, thermal diffusivity, and coefficient of thermal expansion. They are thus considered as replacements for protective coatings or multilayered structures in a number of heat-shielding applications, including reentry space vehicles, space structures, and fusion reactors.[5] The results indicate that, for the same total amount of ceramic phase, the heat-shielding capacity is enhanced by increasing the concentration of the ceramic phase at the heated surface. The temperature gradients inside such a plate are affected by the concentration profile of the ceramic phase. Wu and coworkers[6] pointed out that laser alloying of a gradient metal–ceramic layer cannot only improve the wear resistance of the layer but also avoid the production of cracks. The particles used as hard ceramic phases and incorporated in the layer varied gradually in volume fraction from the surface to the substrate. In the region where the coating material connected with the substrate, good strength was obtained. The layer produced had a gradient structure and excellent bonding with the substrate and was free of pores and cracks. The microhardness of the gradient layer varied smoothly according to the volume variation of the hard ceramic phases.

However, although in science databases there are more than 1,200 publications corresponding to the key words of "gradient and composite," there are only 29 if "poly" as added as a checking term, of which there are few closely related to solid polymer-matrix metal or ceramic gradient composites. In our group, a metal-in-polymer gradient composite was synthesized by solution reduction synthesis.[7–10] In its cross section, the concentration of copper continuously and gradually changes. And surprisingly the deposited metal in polymer matrix has a micromorphology of the metal phase as a three-dimensional network, which interpenetrates with the network of polymer matrix. TEM

results indicated that the metal network was assembled by metal nanoparticles with a diameter of 50 nm.[7] Actually, the formation of the micromorphology comes from the transport and reduction of metal ions (i.e., Cu^{2+}) under an electric field.

Effective ion transport occurs in a swelling cathode film (SCF), where metal-ion-contained polymer matrix is somewhat swollen by residual solvent. Obviously, chemical and physical interactions among polymer groups and metal ions in SCF affect the ion transport. From this point of view, the ion transport in SCF is similar to lithium ion motion in polymer electrolyte in rechargeable lithium batteries.[11–13] On the other hand, electrochemical conditions like a voltage drop in the SCF are important influencing factors on ion transport. Moreover, the liquid electrolyte between the SCF and an anode has a very important influence on the electrochemical process and the morphological structure of gradient film.[7,8] The acidity of a liquid electrolyte actually affects both the concentration of hydrogen ion in liquid electrolyte and further ion-reduction in the SCF.

The ion reduction in SCF is also quite different from a normal electrolytic cell (NEC). In an NEC, the occurrences of electron-acceptance and ion-reduction are on the surface of the cathode, whereas in SCF the ion reduction is probably on the frontier of the deposited metal phase, where the minienvironment of electrochemistry defines the reaction. The hygroscopicity of polymer, possible formation of a complex between functional groups in polymers and metal ions, acidity nearby, etc., are important contributions to the minienvironment.

Based on the above considerations, for this paper, we investigated the effects of (1) the chemical structure of copolymers, (2) the hydration status of polymer groups, and (3) the acidity of liquid electrolyte in an electrochemical reactor, on ion transport and reduction in SCF and morphology of such a composite.

EXPERIMENTAL

Materials

Commercial ternary poly[acrylonitrile (AN)-co-methyl acrylate (MA)-co-sodium allyl sulfonate (SAS)] (93 wt % AN, 6 wt % MA, and 1 wt % SAS) was provided by Zibo Synthetic Fiber Factory, Zibo, People's Republic of China). Reagent-grade N,N-dimethylformamide (DMF) was purchased from Guangzhou Xinjing No.2 Chemical Factory (People's Republic of China) and used as received. Reagent-grade copper chloride was purchased from Tianjin No.2 Chemical Factory (People's Republic of China). It was dried overnight at 105°C to eliminate absorbed and crystal-bound water before use. The monomers used in the syntheses of

copolymers were reagent-grade AN purchased from Shanghai No.3 Chemical Factory (People's Republic of China), reagent-grade MA purchased from Shanghai Henda Chemical Limited Company, People's Republic of China), and sodium allyl sulfonate provided by Zibo Synthetic Fiber Factory. Correspondingly, AN was distilled at 72–73°C and MA at 80–81°C, and SAS was used as received.

Syntheses

Both P(AN-co-MA) and P(AN-co-SAS) were synthesized by an aqueous phase method. $NaClO_3$-Na_2SO_3 were initiators and the polymerization was done at 30–50°C for 5–6 h.

All samples of copper-in-copolymer gradient composite films (CPGCF) were prepared by the electrochemical method, which was roughly similar to our previous studies[7–10] with slight modifications. The method consisted of three basic steps: first, copolymer and copper ions (Cu^{2+}) were dissolved in DMF at 90 ± 2°C in the same vessel for at least 12 h; second, the solution was coated on the upper surface of a disk cathode (Fig. 1). After about 24 h at ambient temperature, an SCF was obtained. Third, the SCF was reduced electrochemically under the proper electrochemical conditions: constant temperature (40°C), 5 h reaction time, and a constant power voltage (1.8 V). The SCFs were predried for 18 h before reduction.

The electrochemical reactor is shown in Figure 1. The anode was a copper disc($\Phi = 38$ mm), and the cathode was a thick carbon disc ($\Phi = 45$ mm) whose upper surface was coated with SCF. The thickness of SCF was about 2.20–2.50 mm. The liquid electrolyte in the electrochemical reactor was an aqueous solution containing Cu^{2+} and H^+. An adjustable DC power supply unit was used to supply the required direct current.

Measurements

The morphological structure of CPGCF was measured by a scanning electron microscope (SEM), JEOL-JSM-840 (Jeol Co., Tokyo, Japan). The method of calculating copper content in film was the same as was employed in our previous study.[7] The compositions of both P(AN-co-MA) and P(AN-co-SAS) were confirmed by a Fourier transform infrared spectrum and ^{1}H-NMR. For IR spectrum measurements with the spectrometer, MAGNA-IR 550 (Nicolet Co., Madison, WI), the copolymer samples were ground into powder and dried at 105°C for 3 h before being mixed with KBr and pressed into pellets. ^{1}H-NMR (ECP-600, Jeol Co., Tokyo, Japan) was used to measure the ratios of different components of copolymer samples. Deuterated N,N-dimethylformamide (DMF-D7) was used as the sol-
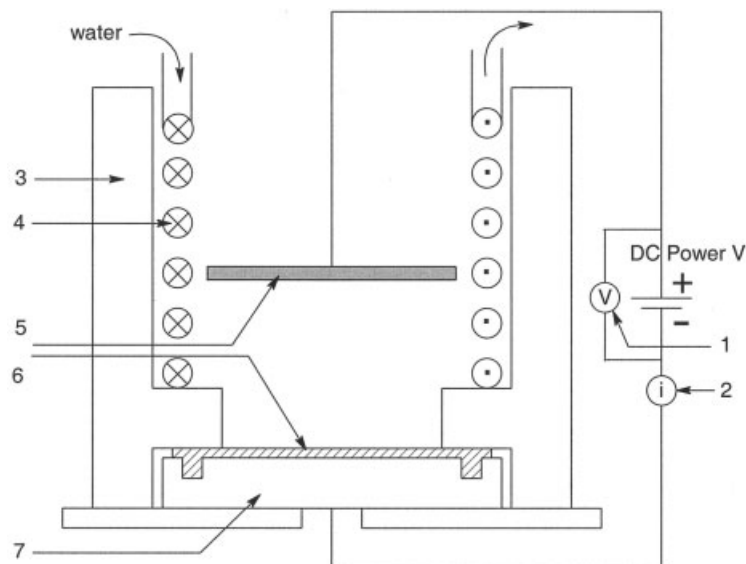
Figure 1 Schematic of electrochemical reactor. It works under DC power supply. On a horizontal cathode (7) a metal ion-containing swelling polymer film was prepared by predrying the solution coating. The space between SCF and anode in this electrochemical reactor was filled with liquid electrolyte, which includes electrochemical active components. Water as cooling medium goes through a helical glass tube. The parts are numbered as follows: (1) voltage meter, (2) current meter, (3) cylindrical wall, (4) helical glass tube, (5) anode, (6) SCF, and (7) carbon cathode.

vent for P(AN-*co*-MA) and deuterated dimethylsulfoxide (DMSO-D6) was the solvent for P(AN-*co*-SAS). The molecular weights of the samples were measured by a viscosity method, according to the Mark-Houwink equation in which $K = 3.21 \times 10^{-2}$ and $\alpha = 0.750$,[7] with dimethylsulfoxide (DMSO) as solvent, at $20 \pm 1°C$.

RESULTS AND DISCUSSION

Confirmation of copolymer compositions

The FT-IR spectrum of P(AN-*co*-MA) is shown in Figure 2 and the assignment of vibration bands are described in Table I. The stretching vibration at 2,244 cm^{-1} of $C\equiv N$ in acrylonitrile and the stretching vibration at 1,737 cm^{-1} of $C=O$ in methyl acrylate confirm the existence of AN and MA in the copolymer. The ^{1}H-NMR of P(AN-*co*-MA) was shown in Figure 3. The signals at $\delta 3.70$, 3.49, and 2.0 ppm are assigned to –CH–CN, –COOCH$_3$, and –CH$_2$–, respectively. The CH–CN signal represents AN units and the –COOCH$_3$ signal indicates MA units, respectively. The molar ratio of AN : MA, which was calculated by comparing their ^{1}H-NMR integral areas, is equal to 9.28 : 1.00. The result of molecular weight measurement indicates that the viscosity average molecular weight [$M(v)$] of P(AN-*co*-MA) is 5×10^4 g/mol.

Similarly, the composition of poly(acrylonitrile-*co*-sodium allyl sulfonate) also was characterized by FT-IR (Fig. 4) and the assignments of vibration bands are

described in Table II. This is the evidence that the copolymer contains sodium allyl sulfonate. The ^{1}H-NMR of poly(AN-*co*-SAS) is shown in Figure 5. The chemical shifts of the sample show signals at $\delta 5.026$–5.059 ppm for –CH$_2$–SO$_3$Na, $\delta 3.17$–3.18 ppm for –CH–CN, and $\delta 2.2$–2.0 ppm for –CH$_2$–: the first two signals
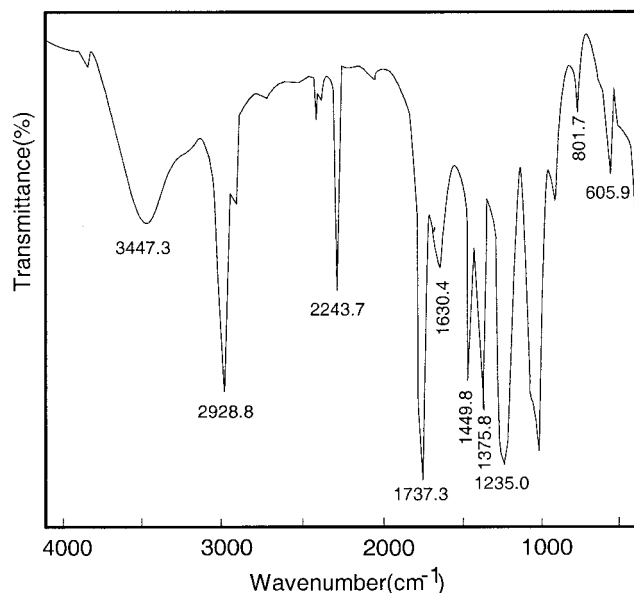
Figure 2 Fourier transfer infrared spectrum of P(AN-*co*-MA). The sample was synthesized in an aqueous condition. NaClO$_3$-Na$_2$SO$_3$ was initiator of this copolymerization. The entire reaction was carried out at $40 \pm 3°C$ for 5 h.
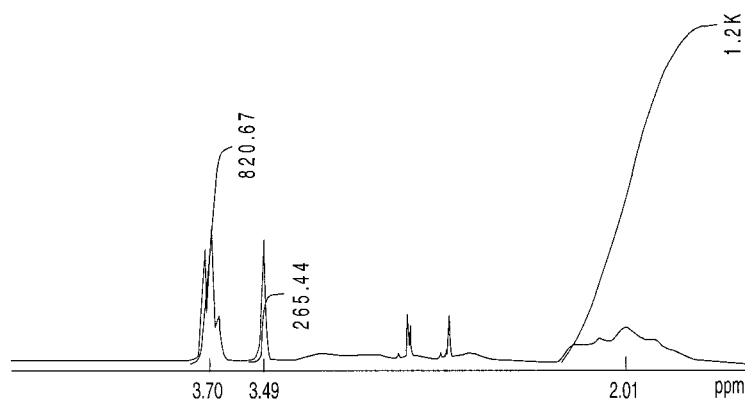
TABLE I
The FT-IR Spectra of Poly(acrytonitrile-*co*-mathyl acrylate)

Vibration band (cm^{-1})	Vibration characterization
1,376	CH$_3$ wagging
1,630	OH stretching
1,737	C=O stretching
2,244	C≡N stretching
2,928	CH asymmetric
3,447	OH stretching

support the copolymer structure of –CH–CN and –SO$_3$Na. The molar ratio of AN : SAS should be 70.5 : 1.00 according to the calculation of ^{1}H-NMR integral areas. The $M(v)$ of poly(AN-*co*-SAS) is 9×10^4 g/mol.

Effects of methyl acrylate and sodium allyl sulfonate on morphology of CPGCF

As a basic component, acrylonitrile is a polar monomer unit in copolymer main chains. Its hydrophilicity is governed by the presence of the nitrile polar group. Van Krevelen's publication[14] gives the stoichiometric evaluation of water absorbance of nitrile. At a relative humidity of 100%, a nitrile group binds 0.3 water molecules. In this paper, the comonomers of methyl acrylate and sodium allyl sulfonate are polar due to their carboxyl ester groups and sulfonate groups, respectively. Since the polarities of carboxyl ester groups and sulfonate groups are definitely different, their hydrophilicities are different. The sulfonate group is a stronger water-absorber. Figure 6 indicates the percentage of copper deposition phase in the cross section of CPGCF via the composition of the mixtures of P(AN-*co*-SAS) and P(AN-*co*-MA). The data were observed by a stereo-optical microscope and were calculated in the width of deposited phase over the entire thickness of CPGCF. The data with 0% of copper deposition, obviously, is for pure P(AN-*co*-MA) ma-

Figure 4 FTIR spectrum of poly(AN-*co*-SAS). The sample was synthesized in an aqueous condition. NaClO$_3$-Na$_2$SO$_3$ was initiator of this copolymerization. The entire reaction was carried out at 40 ± 3°C for 5 h.

trix. The data for pure P(AN-*co*-SAS) matrix shows 49% copper deposition. Between them, the data show how the copper deposition phase changes with the composition of copolymer mixtures: the maximum, 90%, of copper deposition percentage is at the ratio of 1 to 1 (i.e., 50%). This result confirms that copper gradient morphology in polymer matrices is highly related to the content of the stronger water-absorbant copolymer, P(AN-*co*-SAS), but is not a simple proportional relationship. The water absorbance of sodium allyl sulfonate is because of the –SO$_3^-$-chargeable property and the requirement of electroneutrality in SCF to contain charge-compensating ions (Na$^+$) (exchangeable). In contact with an aqueous phase, both nonexchangeable and mobile ions tend to be solvated.

**Figure 3** ^{1}H-NMR spectrum of P(AN-*co*-MA). The sample was synthesized under the same conditions as in Figure 2.

TABLE II
The FT-IR Spectra of Poly(acrylonitrile-*co*-sodium allyl sulfonate)

Vibration band (cm^{-1})	Vibration character
666	S—C vibration
1,190	S=O vibration
1,634	OH vibration
2,245	C≡N stretching
2,928	CH asymmetric stretching
3,449	OH stretching

The solvation process leads to swelling of the polymer phase, which enhances the mobility of the exchangeable ions. This swelling of the polymer phase is very important to improve solubility and solvation of Cu^{2+} in SCF. The carboxylic ester groups in methyl acrylate do not have this chargeable property and make the polymer less swollen, hence pure P(AN-*co*-MA) as a matrix cannot function well for gradient morphology but it is cooperates well with P(AN-*co*-SAS). In the SAS unit, –SO$_3^-$ is an ionic component and it requires the counterion (i.e., Na$^+$) to be neutralized, which might severely interrupt Cu^{2+} coexistence, when its concentration is at high level, for example, over 50%. The nonexchangeable and nonionic carboxyl ester group in methyl acrylate, which is also a water-absorbant unit,[14] can mitigate this over-charging situation and improve the gradient formation of morphology.

Cu^{2+} reduction and the related crystallization of reduced Cu^0 are other concerns for CPGCF. At the sites of the formation and growth of Cu^0 clusters, two processes are of fundamental importance: (1) the arrival and adsorption of ions at the surface and (2) the motion of these adsorbed ions on the surface. An ion deposited on the surface of a perfect crystal stays on the surface as an ion only temporarily since its binding energy to the crystal is small.[15] It is not a stable entity on the surface, but the possible reduction of the ion and the formation of clusters enhances the stability. The free energy of formation of a cluster of N ions, $\Delta G(N)$, has two components (terms):[15]
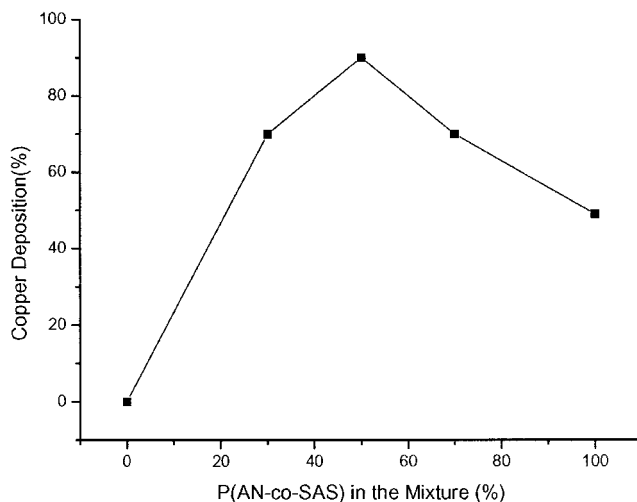
Figure 6 The relationship of the percentage of copper deposition width in the cross section of CPGCF versus the weight percentage of P(AN-*co*-SAS) in the mixture of P(AN-*co*-SAS) and P(AN-*co*-MA). The copolymers of P(AN-*co*-SAS) and P(AN-*co*-MA) were synthesized in an aqueous condition. NaClO$_3$-Na$_2$SO$_3$ was initiator of copolymerization. The entire reaction was carried out at 40 ± 3°C for about 5 h.

$$\Delta G(N) = -Nze|\eta| + \varphi(N) \qquad (1)$$

where η is overpotential, N is the number of transfer ions, z is the electronic charge of ionic species, and e is the charge of the electron. In eq. (1), the first term is related to the transfer of N ions from SCF to the crystal phase and the second term is related to the increase of the surface energy due to creation of the surface of a cluster. This increase of the surface energy, or this excess energy, is equal to the difference of the binding energies of N bulk ions and N ions as arranged on the surface of the crystal. In principle, the occurrence of the swelling of polymer phase is so helpful to decrease the energy of the transfer N ions in SCF that ΔG becomes more negative in the first term in eq. (1). For the second term, the increase of surface energy raises the energy level
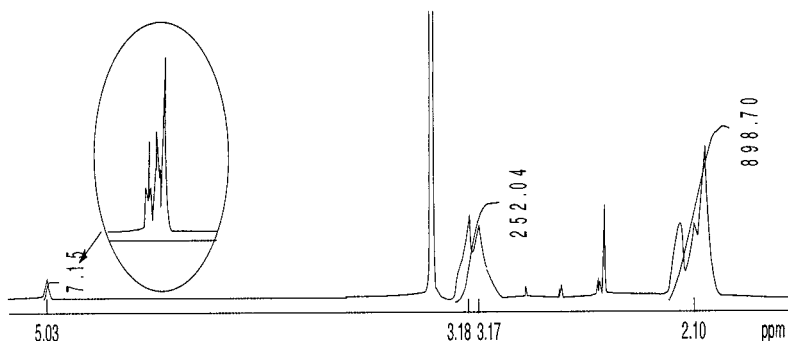
Figure 5 ^{1}H-NMR spectrum of poly(AN-*co*-SAS). The sample was synthesized under the same conditions as in Figure 4.
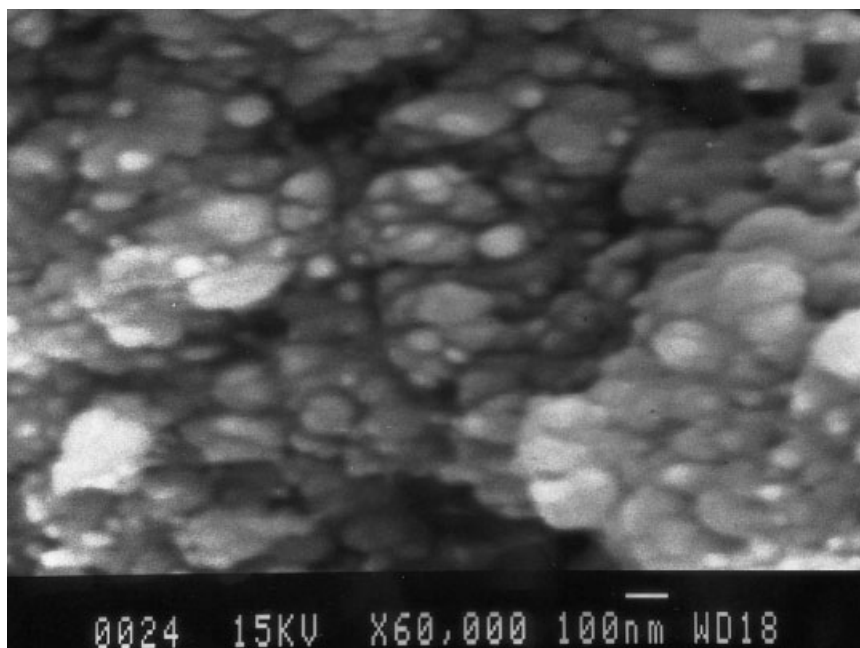
Figure 7 SEM micrograph of nanoparticle-assembled layer of deposited copper phase in ternary copolymer of poly(AN-*co*-MA-*co*-SAS). The pH in liquid electrolyte was −0.17.

and makes ΔG more positive. The process balance, to get ΔG to be close to zero, allows the size of clusters to be 50–100 nm (Fig. 7). This coincides with our previous data.[7]

Effect of acidity of the liquid electrolyte between SCF and anode

Figure 8 indicates the morphological difference due to the change of H^+ concentration in the liquid electrolyte. For the case of pH −0.17, the deposited copper phase has a tree-form structure [Figure 8(1)], while, when pH is 3.5, it becomes a particle-assembled layer of deposited copper. Obviously, acidity in the liquid electrolyte in the electrochemical reactor has an important effect on the morphology of CPGCF.

Figure 9 depicts the relationship between the current in the electric loop and electrochemical reaction time with the influence of different acidities in liquid electrolytes in the electrochemical reactor. Curves (1), (2), and (3) correspond to pH −0.78, −0.17, and 3.5, respectively. Except for the unstable start within the first half minute, the three curves descend gradually with a similar trend. They show minimal currents at about 50 min, which correspond to the order of (1) < (2) < (3). In this period, two electric double layers between cathode and SCF and between SCF and liquid electrolyte were correspondingly established. After 50 min, the electrochemical reductions of SCF showed different current trends. Curves (1) and (3) became horizontal

lines with only some slight fluctuations, whereas Curve (2) was climbing, which means there are more active electrochemical reaction processes occurring within this SCF. Considering also Figure 8(1), the tree-form Cu morphology was obtained at this acidity (pH −0.17). Thus, we can comment that a more active electrochemical reaction after 50 min produces better gradient morphology of deposited copper phase in polymer matrix. H^+ accumulates in the electric double layer between SCF and liquid electrolyte in the process of electric double layer formation in the first 50 min. It affects the ionic motions and electrochemical reaction of Cu^{2+} within SCF through its penetration into SCF and changes in the chemical environment.[16] Actually, the hydrated ions, in liquid electrolyte solution in the electrochemical reactor including Cu^{2+} and H^+, move toward the SCF surface under the drive of the electric field and accumulate outside the SCF surface. These accumulated ions have the tendency to go into the SCF because of the driving force of electric field and concentration gradient. The incoming ions, together with those that have stayed inside, form the environment for electrochemical reduction of Cu^{2+}. The higher current value in the later period of electrochemical reaction [Figure 9[2]] means more active motion of ions in SCF and thus greater reduction of Cu^{2+}. As expected, tree-form morphology is preferred to show the gradient component distribution of copper.
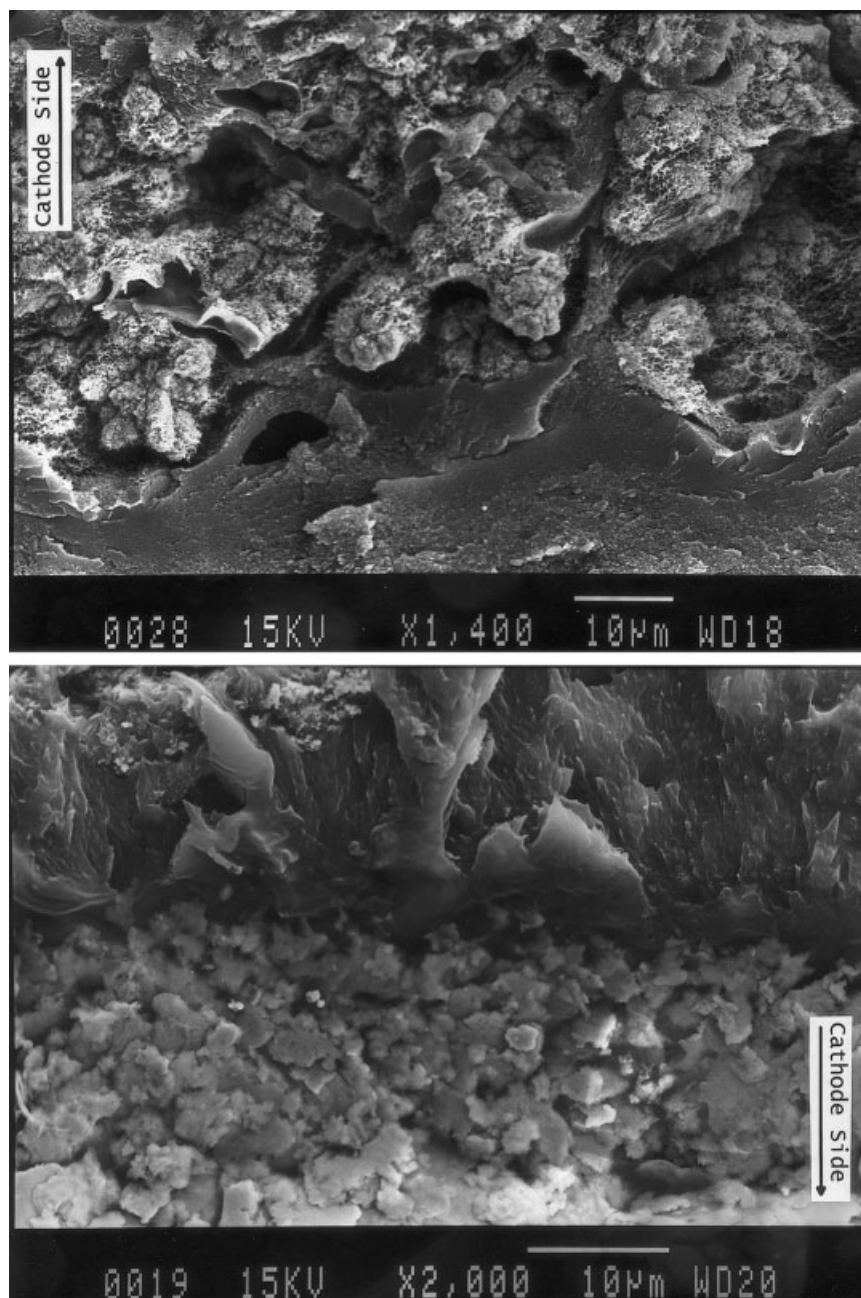
Figure 8 SEM micrograph of deposited copper phase in ternary copolymer of poly(AN-*co*-MA-*co*-SAS). The pH in liquid electrolyte was (1) −0.17 and (2) 3.5.

500CONCLUSION

Gradient materials not only endow either side a different function but also provide an ideal solution to dissolve various kinds of interface problems. The improvement of minienvironment electrochemistry within a SCF and the adjustment of liquid electrolyte are key factors to obtain an ideal gradient morphological structure. Polymer components, obviously, are the most significant part of SCF and hence affect the minienvironment electrochemistry. Through improving the hydrophilicity of copolymers, the swelling of polymer phase and thus the mobility of the exchangeable ions in a SCF can be increased. The ionic group, $-SO_3^-$, plays an important role for this swelling of the polymer phase. The carboxylic ester groups in methyl acrylate do not have this ionic property, so that pure P(AN-*co*-MA) as a matrix cannot function well for copper deposition and gradient morphology, although it is a cooperative component with P(AN-*co*-SAS), when its concentration is at a high level (e.g.,
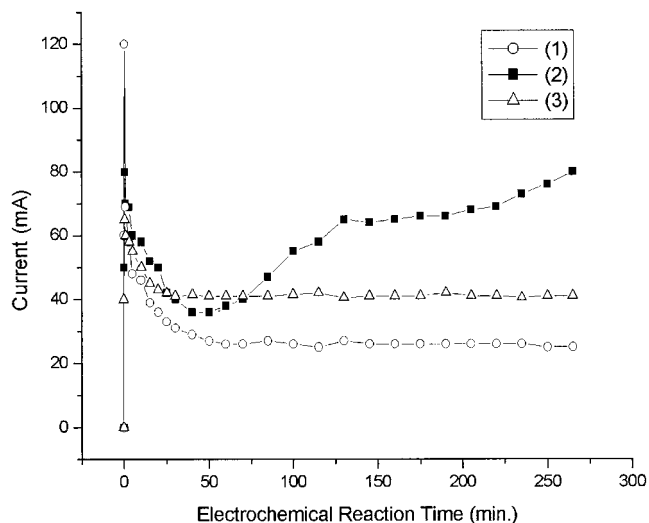
Figure 9 The effect of different H^+ concentrations in liquid electrolyte on current. The pH in liquid electrolyte was (1) −0.78, (2) −0.17, and (3) 3.5.

over 50%). Swelling of the polymer phase is helpful to decrease the energy of the transfer ions in SCF. The increase of surface energy because of cluster growth enhances the energy level and makes ΔG more positive. The appropriate H^+ concentration improves Cu^{2+} reduction in the later period of electrochemical reaction and gradient morphology of the deposited copper phase in a polymer matrix.

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