

# Poly(dimethylaminoethylmethacryloylpropanesulfonate)-Suitable Polymer Additive for Pulsed Electrodeposition of Nanocrystalline Nickel

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**ABSTRACT:** Nano-nickel (*n*-Ni) is deposited by a pulsed electrodeposition (PED) in the presence of nonionogenic (poly(ethylene glycol), poly(*N*-vinylpyrrolidone), starch), anionogenic (gum arabic, sodium alginate), cationic (quaternized guar gum), and polyampholytic (polyzwitterionic) poly(dimethylaminoethylmethacryloylpropanesulfonate) (PDMAEMPS) polymers. It is established that, by PED (40 mA/cm<sup>2</sup>,  $t_{\text{on}} = 1$  ms,  $t_{\text{off}} = 50$  ms, 323 K), the size of the nanocrystalline particles produced in the presence of PDMAEMPS is far less (by a factor of 6–10) than those obtained in the presence of other polymer additives. These

comparative results emphasize a new possibility of controlling the nanograin size of the electrodeposited metals by PED. The dramatic difference in the size of the nickel particles and the unique ability of the polyzwitterionic (PZI) additives are connected by the specific for the polyzwitterionic macromolecular conformation response to the pulsatile electric potential. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2967–2971, 2006

**Key words:** pulsed electrodeposition; polyzwitterion; polymer additive; saltphilicity

## INTRODUCTION

Nanostructured metals exhibit very important physical properties, different from those of bulk metals.<sup>1–5</sup> For this reason, numerous methods have been developed for their preparation.<sup>6–9</sup> Among them, pulsed electrodeposition (PED) is distinguished by its cost efficiency, versatility, reliability, and possibility for industrial applications.<sup>10,11</sup> In the PED technique, the deposition rate is governed by four important current parameters:  $t_{\text{on}}$  time,  $t_{\text{off}}$  time,  $I_{\text{pulse}}$ , and  $I_{\text{a}}$  (Fig. 1). The  $t_{\text{on}}$  time is the length of a current pulse, the  $t_{\text{off}}$  time is the time between two pulses,  $I_{\text{pulse}}$  is the pulse height, and  $I_{\text{a}}$  means the average current density. The first approach for grain size reduction is an electroplating with short  $t_{\text{on}}$  times, combined with high peak current density. For the  $t_{\text{off}}$  time, one has to compromise; it has to be as long as necessary to enable material transport into the depleted vicinity of the cathode, and it has to be as short as possible in order to minimize grain growth due to the exchange current density; smaller grains dissolve and larger grains grow preferentially.

Nanocrystalline nickel (*n*-Ni) has already been prepared using PED.<sup>12–16</sup> It is commercially applied for the in situ repair of nuclear steam generators in the so-called Electrosleeve<sup>TM</sup> process.<sup>17</sup> Despite the peculiarities of the used procedure,<sup>12,13</sup> the method does not allow the deposition of particles with a grain size of < 25 nm. Using the electrolyte bath consisting 40 g/L NiSO<sub>4</sub>, 60 g/L K, Na-tartrate, 20 g/L NH<sub>4</sub>Cl, this size can be varied between 25 and 44 nm, by changing  $t_{\text{off}}$  time between 5 and 249 ms at constant  $t_{\text{on}}$  time (1 ms) and  $I_{\text{a}} = 5$  mA/cm<sup>2</sup>. However, with regard to fundamental studies of the quantum size effect, e.g., with quantum diffusion of light interstitial atoms or with phonon confinement, as well as with regard to possible applications, particles with a grain size of < 20 nm and without texture are required. For this reason, it is interesting to study the influence of the polymer additives to the electrolyte bath. To the best of our knowledge, hydrophilic polymers are not tested so far as additives, inhibitors, and stabilizers. At the same time, these polymers, and especially polyelectrolyte additives, can have a considerable influence on the local ion concentration, bath viscosity and ion mobility, adatom surface diffusion, and adsorption on the electrode surface and on the active sites. In the present contribution, the influence of hydrophilic polymers of various types as additives to the PED bath on the grain size distribution of the produced *n*-Ni is tested for the first time. The

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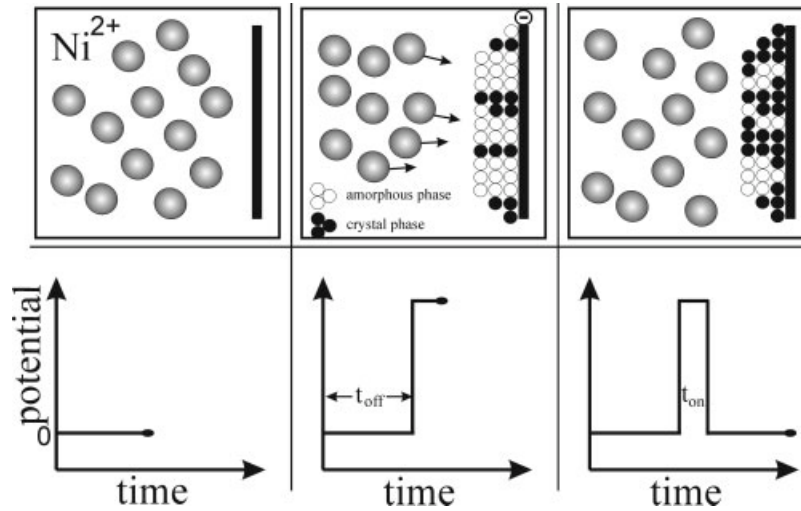


Figure 1 Potential changes during the nickel PED.

considerable positive effect of the polyzwitterionic additive (polymer with a macromolecular conformation strongly dependent on the electrical potential value and salt concentration) on the *n*-Ni grain size is shown.

## EXPERIMENTAL

The nanocrystalline nickel was deposited on stainless cathodes (20 × 30 mm, 1 mm thick). The modulated currents were generated by a signal generator, which controls a bipolar operation source, combined with a galvanostatic unit in order to keep the peak current at a constant value during the pulse.<sup>16</sup> In PED used in this case, the peak current density is very high (40 mA/cm<sup>2</sup>), the *t*<sub>on</sub> time is 1 ms, and the *t*<sub>off</sub> time is 50 ms (Fig. 1). A double-walled glass plating cell (250 ml) enables the electrolysis at a constant temperature of 323 K. The electrolyte bath consists of 40 g/L NiSO<sub>4</sub>, 60 g/L K, Na-tartrate, 20 g/L NH<sub>4</sub>Cl, and 0.2 g/L hydrophilic polymer additive. The electrolyte was stirred mechanically. The oxygen dissolved in the electrolyte was expelled with a stream of nitrogen (2 h). A nickel electrode was used as anode so the anodic reaction is the dissolution of nickel; oxygen evolution is avoided in this way and the Ni<sup>2+</sup> concentration does not change with time. The XRD-measurements were performed using a Siemens D-500 diffractometer in 2θ-mode with secondary monochromatic copper radiation. The 2θ angle was calibrated with a LaB<sub>6</sub>-standard sample (NIST). The volume and area weighted grain size, grain size distribution, and microstrain can be obtained from the analysis of the X-ray diffraction line shape. For this reason, a slightly modified method of Warren and Averbach<sup>17–20</sup> was used. The method is a Fourier method, allowing the separation of size and strain effects on the grain-size distribution. In order to

smoothen the data, every relevant diffraction peak is fitted with a Pearson VII function, and then the resulting fit function is Fourier transformed. The Fourier coefficients of the scattering function are the products of both size and strain terms:

$$A_n^{\text{hkl}} = A_n^{\text{size}} A_n^{\text{strain}}(\text{hkl}). \quad (1)$$

The size term does not depend on hkl, whereas the strain does; this allows their separation. Fourier coefficients versus  $d_{\text{hkl}}^2$  ( $d_{\text{hkl}}$  is the corresponding interplanar distance) yields the strain-corrected coefficients  $A_n^{\text{size}}$ . Subsequently, the normalized strain-corrected Fourier coefficients  $A_n^{\text{size}}$  are plotted versus column length  $L = nd^*$ , where  $n$  is the number of the Fourier coefficient, and  $d^*$  is the fictitious interplanar distance. From the initial slope at  $L \rightarrow 0$  and from the integration of the  $A^{\text{size}}$  vs.  $L$  dependence, the area-weighted average and volume-weighted average column lengths, respectively, are obtained:

$$dA^{\text{size}}/dt|_{L \rightarrow 0} = -1/\langle L \rangle_{\text{area}} \quad (2)$$

$$\int_0^{\infty} A^{\text{size}} dL = \langle L \rangle_{\text{volume}}/2 \quad (3)$$

For spherical shape particles, the relation between column length and diameters is given by

$$\langle D \rangle_{\text{area}} = 3/2 \langle L \rangle_{\text{area}} \quad (4)$$

$$\langle D \rangle_{\text{volume}} = 4/3 \langle L \rangle_{\text{volume}} \quad (5)$$

The last equation was used for the determination of the volume averaged particle diameters in this work (Table I). From these two average diameters, it is

**TABLE I**  
**Volume Averaged Grain Diameter ( $\langle D \rangle_v$ ) and Size Distribution Relative Width ( $\sigma$ ) of the Nanocrystalline Nickel Produced with and without Different Hydrophilic Polymers as Additives**

N	Polymer additive	$\langle D \rangle_v$ (nm)	$\sigma$
1	PEG <sub>4000</sub>	49.8	1.07
2	PEG <sub>20000</sub>	39.3	1.39
3	PNVP	35.1	1.38
4	S	50.1	1.67
5	GA	32.3	1.43
6	SA	32.5	1.41
7	GGC	36.8	1.42
8	PZI	5	—
9	Blank	41.2	1.45

possible to determine the parameters of the log-normal grain-size distribution:

$$g(d) = [1/(2\pi)^{1/2}D\ln\sigma] \exp\{-1/2[\ln(D/\mu)/\ln\sigma]^2\} \quad (6)$$

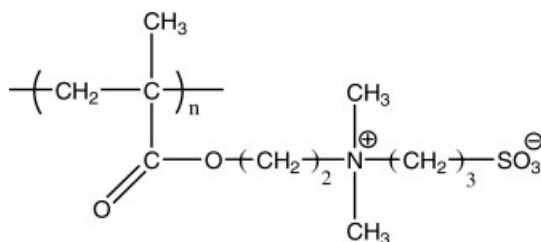
via the next two relationships:

$$\mu = \langle D \rangle_{\text{area}}^{7/2} \langle D \rangle_{\text{volume}}^{-5/2} \quad (7)$$

$$\sigma = \exp(\ln\langle D \rangle_{\text{volume}} / \langle D \rangle_{\text{area}})^{1/2} \quad (8)$$

The results obtained from the last equation are included in Table I as well.

The effect of four types of hydrophilic polymers was compared: nonionogenic, polyanionic, polycationic, and polyampholytic ones. Poly(ethylene glycol) with molecular weight 4000 (PEG<sub>4000</sub>) and 20000 (PEG<sub>20000</sub>) (FLUKA), poly(*N*-vinylpyrrolidone)-30 K (PNVP) with molecular weight 40000 (FLUKA), and starch (S) (ABCR GmbH) were used as nonionogenic polymers. The natural gum Arabic (GA) and sodium alginate (SA) (ABCR GmbH) are the used polyanions. Polycations are represented by a guar gum quaternized with 2-hydroxy-3-(trimethylammonium)propyl chloride (GGC; Rhodia Inc.). The synthesized poly(dimethylaminoethylmethacryloyl propanesulfonate) (PDMAEMPS) is used as polyampholyte:



The first three types of the polymer additives were commercial products and used as received. PDMAEMPS was synthesized by a method described earlier.<sup>21</sup> After its purification by the precipitation (ace-

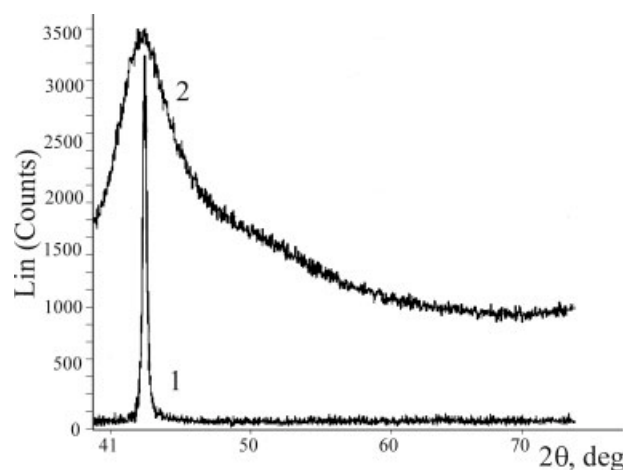
tone)-solvation (water) procedure and drying at 55°C under vacuum, its molecular weight was determined ( $M_w = 76,000$ ) by the laser-scattering method (Malvern Systems 4700-E).

## RESULTS AND DISCUSSION

Figure 2 compares the X-ray diffractograms of *n*-Ni produced with PEG<sub>20000</sub> (curve 1) and PDMAEMPS (curve 2) as additives. The dramatic difference between them is evident. Crystalline nickel nanoparticles with low grain size are only produced with PZI as additive. X-ray diffraction patterns similar to that with PEG<sub>20000</sub> are recorded for *n*-Ni produced with PEG<sub>4000</sub>, PNVP, S, GA, SA, and GGC and without polymer additive. The volume averaged particle diameters [ $\langle D \rangle_v$ , eq. (5)] and relative width [ $\sigma$ , eq. (8)] of the calculated grain size distribution from these diffractograms are presented in Table I.

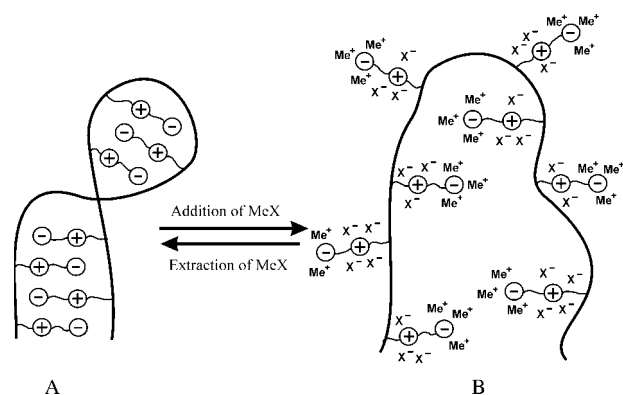
Among the hydrophilic nonionogenic polymer additives (PEG<sub>4000</sub>, PEG<sub>20000</sub>, PNVP, and S) PNVP is the most favorable for the  $\langle D \rangle_v$  decrease, as compared with the  $\langle D \rangle_v$  value produced without polymer additive (No. 9 in Table I). The PEG molecular weight increase is a positive factor in the same direction. The transition from the nonionogenic polymers (additives 1-4) to the polyanions (additives 5 and 6) also contributes to the  $\langle D \rangle_v$  decrease. This effect could be related to the polyanion-nickel cation complex formation in the bath. The polycationic (additive 7) has an effect on  $\langle D \rangle_v$ , which is approximately the same as that of PNVP. As can be seen in Table I, the above-mentioned considerable difference between the X-ray diffractograms (Fig. 2) is expressed as a  $\langle D \rangle_v$  decrease by a factor of 6–10, as compared with the other hydrophilic polymer additives.

The result obtained could be explained by the specific PZI macromolecular structure organization. In the

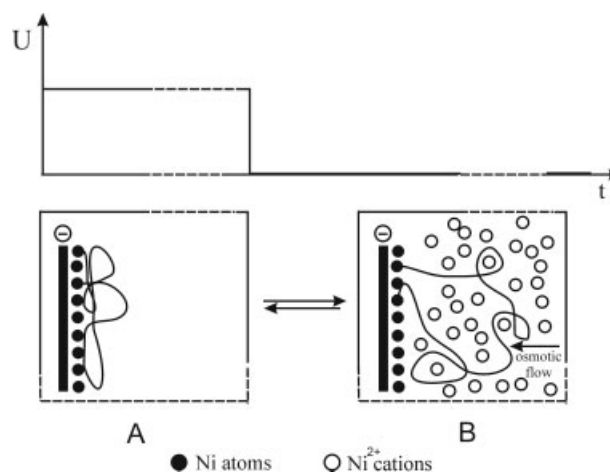


**Figure 2** X-ray diffractograms of *n*-Ni produced with PEG<sub>20000</sub> (curve 1) and PDMAEMPS (curve 2) as additives.

absence of the low-molecular salt (MeX), the PZI macromolecule is in the compact globular conformation state due to the interaction between the opposite oriented dipoles on the monomer units [Fig. 3(A)]. These dipole clusters play the role of physical nodes in the macromolecule globules. In the electric field, the dipole orientation changes along the field direction, the physical nodes are destroyed and the macromolecules swell. This swelling was used in our previous work<sup>21</sup> for the explanation of the electroviscosity results obtained. The viscosity of the 0.2 wt % PDMAEMPS aqueous solution increases by a factor of 14.7 under the electrical field with intensity of 6 kV/cm. In the presence of the low-molecular salt, the PZI macromolecule also swells due to the screening effect of the low molecular ions and dipole-dipole interaction diminution [Fig. 3(B)]. This is the reason for the specific "saltphilic" PZI properties and for the increase of their solubility in water.<sup>22</sup> It was shown that the PDMAEMPS dissolution temperature in water (registered through the solution optical transmittance) decreases by 20°C in the presence of 0.1 wt% NaCl. In the swollen state [Fig. 3(B)], the adsorbed on the cathode PZI macromolecule plays the role a local Ni<sup>2+</sup>-concentrating reservoir. The latter is filled with nickel salt at zero value of the cathode potential during the nickel PED [Fig. 4(B)]. It provides a considerable local Ni<sup>2+</sup> supersaturation, necessary, according to the theory,<sup>23</sup> for the production of many low-size grains. Turning on the bias voltage, the PZI macromolecule adsorbed on the cathode pushes away the Ni<sup>2+</sup> cations and passes into the globular state (from the solution) [Fig. 4(A)]. During the next potential elimination, new Ni<sup>2+</sup> cations enter in the globule forced by the osmotic strength. The macromolecule swells, and it again becomes the Ni<sup>2+</sup> reservoir near the cathodes surface, ready for the next working cycle. The extremely high efficiency of PZI as additive could be connected with this specific macromolecular conformation response to the pulsatile electrical potential. As a result, an additional influence on the concentration of



**Figure 3** Fragment of the PZI macromolecular globule in the absence of the low molecular salt (MeX) (A), and its swelling in the presence of the same salt (B).



**Figure 4** Schematic representation of the PZI macromolecular conformation change between the compact globular state under an external electrical potential (A) and a swollen cation state, filled in Ni<sup>2+</sup> when the external potential is zero (B).

growth sites (the atoms on the cathode surface), on their diffusion coefficients, and on the activation energy of surface diffusion becomes possible.<sup>24</sup> In addition, the macromolecular coating of the growth sites [Fig. 4(B)] could be regarded as a specific grain boundary between the small crystallites. In the presence of the low-molecular-weight zwitterions instead of PDMAEMPS in the bath, such conformation transitions are not possible. Thus, the grain size of *n*-Ni produced in the presence of a zwitterionic monomer is close to those obtained without polymer additives (No. 9 in Table I).

## CONCLUSION

It is proved that PDMAEMPS is the best polymer additive (among the ionic and nonionic polymers tested) for the PED of the nanocrystalline nickel. The size of nanoparticles with these additives is far less than those obtained in the presence of other polymer additives. In this way, PZI additives offer new possibilities for a grain size control during the metal PED. This short communication emphasizes the first place of this experimental result. The proposed qualitative explanation is in accordance with our previous results on the electroviscosity and saltfilling PZI properties. The quantitative investigations in this direction are in prospect.

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