

# Improved electrolyte for zinc-polyaniline batteries

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## INTRODUCTION

Up to now zinc-PANI batteries has not been commercialized from few main reasons. First reason is degradation process of PANI at potentials more positive than  $-0.5$  V [1, 2], and second is zinc passivation, which is possibly related to the formation of the solid phases  $\text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2 \cdot 2\text{NH}_4\text{Cl}$  on the anode surface [3]. On the other hand, in chloride containing electrolytes Zn electrodes form dendrites during charge-discharge cycles [5]. It results in decreased coulombic efficiency of batteries and charge life. Main reason for that are sort circuit provoked by penetration of dendrites through separator to cathode or formation of the anodic slime.

It is well known that some organic anions can form complexes with the metal ions, that results much better quality of the metal deposits and suppress dendrite formation [7]. Probably, the best choice will be oxalic anions, due to the small ionic radius, good PANI doping-dedoping characteristics, etc [8]. Unfortunately, zinc oxalate is an insoluble salt.

In this paper we have investigated behavior of zinc and PANI electrodes in chloride containing electrolytes with addition of citrate anions, which at pH=5 that can form an soluble zinc citrate  $[\text{ZnCit}]^-$  complex.

## EXPERIMENTAL

Polyaniline was obtained from hydrochloric acid solution (0.1 M) with addition of 0.1 M aniline monomer (p.a. Merck, distilled in argon atmosphere), at constant current density of  $1 \text{ mA cm}^{-2}$  on graphite electrode. Electrolytes containing 0.5 M  $\text{NH}_4\text{Cl}$ , 0.20 M  $\text{ZnCl}_2$ , and with addition of 0.33 M Na-citrate were prepared from p.a. grade chemicals (Merck) and bidistilled water. For all experiments three compartment electrochemical cell, with platinum foil ( $S=2 \text{ cm}^2$ ) as a counter and saturated calomel electrode as a reference electrode at room temperature was used. The working electrodes, graphite ( $S=0.64 \text{ cm}^2$ ) and zinc ( $S=2 \text{ cm}^2$ ), were mechanically polished with fine emery papers (2/0, 3/0 and 4/0, respectively) and then with polishing alumina of  $1 \mu\text{m}$  (Banner Scientific Ltd) on the polishing cloths (Buehler Ltd.). After mechanical polishing the traces of polishing alumina were removed from the electrode surface in an ultra-sonic bath during 5 min. The electrochemical measurements were carried using a PAR 273A potentiostat controlled by a computer through a GPBI PCZA interface.

## RESULTS AND DISCUSSION

On Fig. 1. comparison of zinc deposition-dissolution on graphite electrode from chloride and chloride/citrate containing electrolytes are shown. As it can be seen from chloride electrolyte, deposition processes starts at potentials around  $-1$  V, thought one well defined peak, at  $-1.17$  V, after at potentials more negative than  $-1.4$  V proceed simultaneous zinc deposition and hydrogen evolution reactions. In anodic direction, zinc dissolution occurs at potentials more positive than  $-1$  V through one peak and one shoulder. In citrate/chloride electrolyte deposition-dissolution reaction is shifted for  $-0.15$  V in negative direction and diffusion limited peak is two times smaller, than in chloride electrolytes. This behavior could be explained by zinc ions complexation and lowering of the free zinc ions activity, as well as diffusivity of zinc citrate complex comparing with chloride electrolyte.

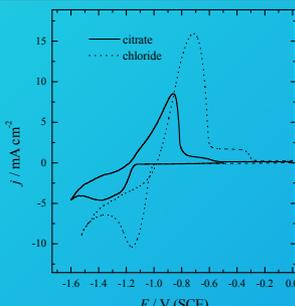


Fig. 1. Cyclic voltammograms of graphite electrode in 1) 0.50 M  $\text{NH}_4\text{Cl}$  + 0.20 M  $\text{ZnCl}_2$  and 2) with addition of 0.33 M Na-citrate. Sweep rate  $20 \text{ mV s}^{-1}$ .

In Fig. 2 micrographs of zinc deposits obtained from chloride and chloride/citrate electrolytes at a constant current density of  $3.5 \text{ mA cm}^{-2}$  and with deposition charges of  $10.5 \text{ mA h cm}^{-2}$  are shown. In chloride electrolyte, Fig. 2a, obtained deposits are practically completely dendritic, so potential risk of fast dendrite growth through separator, during the longer charging times, and formation of short circuits with cathode is permanently present. On the other hand in chloride/citrate electrolyte, Fig. 2b, deposit is smooth without irregularities even in the edges where local current density due to the current distribution phenomena is higher than at the central surface.

Fig. 2. Micrographs of the zinc deposits from a) 0.20 M  $\text{ZnCl}_2$  + 0.50 M  $\text{NH}_4\text{Cl}$  b) with addition of 0.33 M Na-citrate. Deposition current density  $3.5 \text{ mA cm}^{-2}$ , deposition time 3 h, magnification 200 x.

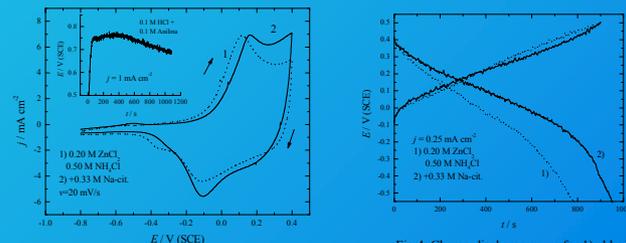


Fig.4. Charge-discharge curve for 1) chloride and 2) chloride/citrate electrolyte at current density of  $0.25 \text{ mA cm}^{-2}$ .

Fig. 3. Cyclic voltammograms of PANI electrode in 1) chloride and 2) chloride/citrate electrolyte ( $v=20 \text{ mV s}^{-1}$ ). Inset: galvanostatic curve for aniline polymerization from 0.1 M HCl and 0.1 M aniline at  $1 \text{ mA cm}^{-2}$  on graphite electrode.

Charging/discharging characteristics of PANI film electrode are affected with applied current density, mainly because chloride anions diffusion limitation through PANI film. On Fig. 5 dependence of capacity during discharge processes for different discharging current densities are shown. Discharge capacity increase with decreasing applied current density and for the limiting case when  $j_d \rightarrow 0$ , discharge capacity has a value of  $0.082 \text{ mAh cm}^{-2}$ . It could be calculated that mass of the PANI on graphite electrode was approximately 0.5 mg. Hence, for the limiting case with discharge capacity of  $0.082 \text{ mAh cm}^{-2}$  specific discharge capacity could estimate on  $165 \text{ mAh g}^{-1}$ . In the range of investigated current densities of 0.25 to  $1 \text{ mA cm}^{-2}$ , specific discharge capacity was in the range of 130 to  $85 \text{ mAh g}^{-1}$ , respectively.

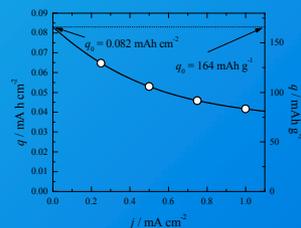


Fig. 5. Dependence of charge (left) and specific charge (right) at different discharge current density for PANI electrode in chloride/citrate electrolyte.

The overpotential and the current density in activation-controlled deposition inside the Tafel region are related by:

$$\eta = b_c \ln(j/j_0) / 2.303 \quad (1)$$

Therefore, increasing  $b_c$  and decreasing  $j_0$  leads to an increase in the deposition overpotential at the constant current density. It follows from all available data that the former effect is more pronounced resulting in deposits with a finer grain size with decreasing value of the exchange current density. This analysis explain differences in deposit morphology for chloride and chloride/citrate electrolytes taking into account that Tafel slopes are  $-35$  and  $-108 \text{ mV dec}^{-1}$ , and exchange current densities are  $0.38$  and  $0.027 \text{ mA cm}^{-2}$ , respectively. Hence, in chloride electrolyte at  $3.5 \text{ mA cm}^{-2}$  deposition overpotential is only  $-30$  V, while in chloride/citrate electrolyte is  $-220$  mV. Polymerization starts at potential of  $0.75$  V and proceed in the potential range between  $0.75$  and  $0.7$  V. After transfer, electrode was conditioned at potential of  $-0.8$  V for 600 s and cyclic voltammograms in the potential range between  $-0.8$  and  $0.4$  V were taken as shown in Fig. 4. In anodic direction doping of the anions occur at potentials more positive than  $-0.2$  V, with pronounced peak at  $0.15$  V. In cathodic direction dedoping of anions occur through one shoulder in the potential range of  $0.4$  to  $0.05$  V and one well defined peak with the maximum at  $-0.1$  V. Dedoping of anions is finished at potentials of  $-0.4$  V. Small differences in the shapes of cyclic voltammograms between chloride and chloride/citrate electrolytes, could indicate that only chloride anions are involved in doping/dedoping reaction.

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