Electrochemical behavior of polyaniline in chloride/citrate electrolyte

B.Z. Jugović[1], M. Gvozdenović[2], T. Lj. Trišović[1], J. Stevanović[3], B.N. Grgur[2]

[1]Institute of Technical Science, Serbian Academy of Science and Arts, Knez Mihailova 35, Belgrade, Serbia
[2]Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia
[3]Institute of Electrochemistry, ICTM, Njegoševa 12 Belgrade, Serbia

INTRODUCTION

Among large number of ECP, polyaniline (PANI) is the most investigated as cathode material in aqueous based electrochemical power sources. Although systems consisted of PANI cathode combined to electronegative metal (mainly zinc) anode, are likely to accomplish most of the three E criteria: Energy (high energy content with respect to volume and weight), Economics (low manufacturing and maintenance costs, long service life), Environment (toxic free, safety, low energy consumption, easy to recycle) elaborated as the determining factors of an electrochemical power system success they still have not been commercialized from several reasons. First reason is related to the fact that PANI is degradable at potentials more positive than 0.5 V, while the main reason is connected to zinc dendrite and solid phase formation during charge/discharge cycles in common chloride based electrolytes, affecting columbic efficacy and cycle life. It was shown previously that addition of citrate anions in chloride electrolyte had resulted in lowering of zinc dendrite formation and corrosion rate. Hence, the aim of this paper was to investigate the influence of citrate anions on characteristic of electrochemically synthesized PANI electrode for potential use in electrochemical power sources.
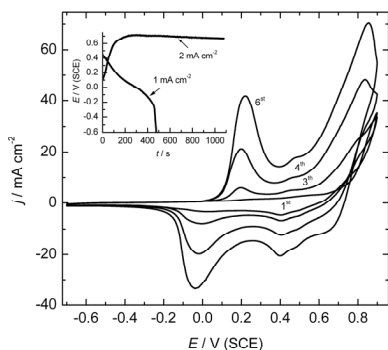
RESULTS AND DISCUSSION

Fig. 1. Galvanostatic curve of electrochemical polymerization of aniline at graphite electrode in 1.0 mol dm^{-3} HCl and 0.25 mol dm^{-3} aniline, j = 2.0 mA cm^{-2}. Insert: Cyclic voltammogram of PANI electrode in 1.0 mol dm^{-3} HCl and 0.25 mol dm^{-3} aniline (v = 20 mV s^{-1}).
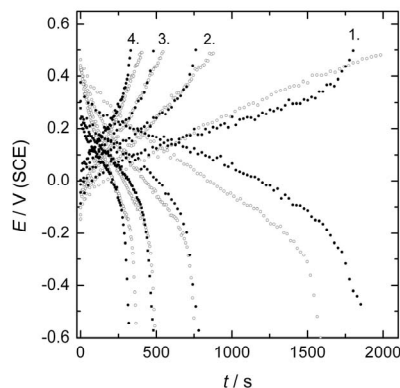

Fig.2. Charge/discharge curves of PANI electrode in (○)-chloride and (●)-chloride/citrate obtained with current densities: 1-0.25; 2-0.50; 3-0.75 and 4-1.00 mA cm^{-2}.
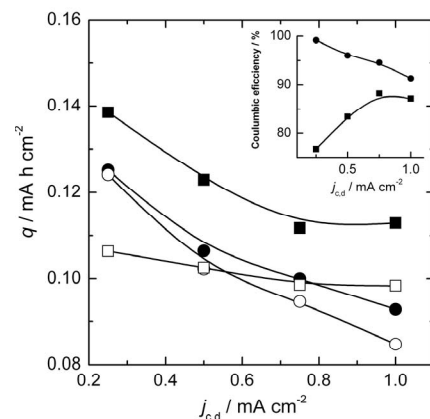

Fig.3. Dependences of charge: (●)-chloride/citrate; (■)-chloride, and discharge: (○)-chloride/citrate; (□)-chloride, capacity of PANI electrode on current density. Insert: Columbic efficiency.
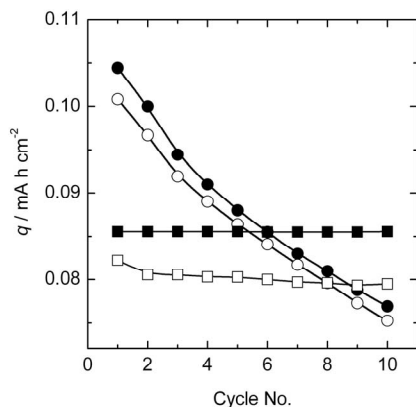

Fig.4. Dependences of PANI electrode capacities on cycle number in chloride/citrate electrolyte, for anodic potential limit of 0.5 V: (●)-charge, (○)-discharge and 0.32V (■)-charge, (□)-discharge. Insert: Columbic efficiency for anodic potential limit of: (●)-0.5 V and (■)-0.32 V.
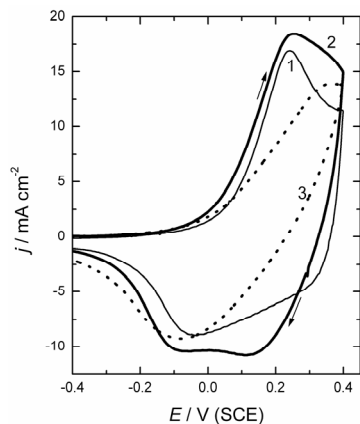

Fig.5. Cyclic voltammograms of PANI electrode in: 1-chloride, 2-chloride/citrate and 3-citrate electrolyte, v = 20 mV s^{-1}.

CONCLUSION

Electrochemical synthesis of PANI on graphite from aqueous solution of hydrochloric acid containing aniline monomer was performed galvanostatically. The polymerization charge was 0.60 mAh cm^{-2} while discharge charge was ~ 0.14 mAh cm^{-2}, so it was concluded that only 23 % of the total polymer mass was available for charge exchange, while rest of the charge refers to formation of inactive PANI oligomers and degradation products. Based on electrochemical studies, it was concluded that in chloride/citrate electrolyte both citrate and chloride anions played role in doping. The faster decrease in charge/discharge capacity in chloride/citrate electrolyte compared to chloride for potential limit of 0.50 V was explained by hydrophilic effect of citrate ions, while higher charge/discharge capacities were explained by negative doping potential shift of about 30 mV. It was recommended that charging potential should not exceed 0.35 V.