Electrochimica Acta 184 (2015) 111–116

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Effect of potential range on electrochemical performance of polyaniline as a component of lithium battery electrodes

Olga A. Kozarenko, Vyacheslav S. Dyadyun, Mykhailo S. Papakin, Oleg Yu. Posudievsky*, Vyacheslav G. Koshechko, Vitaly D. Pokhodenko

L.V. Pisarzhevsky Institute of Physical Chemistry of the National Academy of Sciences Ukraine, 31 prospekt Nauki, Kyiv 03028, Ukraine

ARTICLE INFO

Article history:
Received 30 June 2015
Received in revised form 17 September 2015
Accepted 12 October 2015
Available online xxx

Keywords:
Polyaniline
Electrochemical performance
Potential range
Resistance
Capacity

ABSTRACT

This work studies the dependence of the electrical conductivity of $HClO_4$ doped polyaniline (PAni) on the potential in an aprotic electrolyte (1 M $LiClO_4$ in EC/DMC) and establishes that it possesses a sufficiently high conductivity within a narrow potential range 3.3–3.5 V vs. Li/Li^+, beyond which its resistance increases sharply. It is shown that PAni, as a component of lithium battery electrodes, could be subjected to stable charge-discharge cycling in the 1.0–4.2 V vs. Li/Li^+ potential range and that decrease of the lower limit of the potential range below 1.0 V could lead to the formation of an SEI layer, which causes the irreversible reduction of PAni electrochemical performance.

1. Introduction

It is known that lithium-ion batteries (LIBs) possess high energy density, superior to many other types of commercial batteries [1,2], that attracts attention of researchers to further development of new LIBs. One important incentive is the fact that modern values of specific energy of the commercial LIBs based on conventional electrochemical systems consisting of a lithiated transition metal oxide cathode and a carbon anode (the theoretical specific capacity of graphite is 372 mAh/g) approach their limit. A further increase of energy density of LIBs could be achieved only by replacing the active components of the electrodes with fundamentally new ones [3–15].

Many materials capable of electrochemical intercalation of lithium ions at sufficiently low potentials vs. Li/Li^+ are known [2,5,7,9,11]. Recently, Si, Ge, Sn, SnO_2, TiO_2, $Li_4Ti_5O_{12}$, Li_3VO_4, Fe_3O_4, MoS_2, graphenes and so on [2,5,7,9,11] were considered as an alternative to carbon anodes. Such materials have a number of advantages relative to the commercially used carbon electrodes, particularly a greater specific capacity and higher rate capability (in the case of $Li_4Ti_5O_{12}$). However, many of them possess inherently weak structural stability during charge-discharge cycling, as well as relatively low values of conductivity [2,5,7,9,11]. To overcome these disadvantages, the active anode material particles are coated with carbon [16–20], various metals [21–23] or conducting polymers (CP) [24–27]. Among CP, many authors try to use polyaniline (PAni) as a perspective coating [28–39]. Some results devoted to the usage of PAni in anodes of LIBs are presented in Table 1.

The authors of [28–39] use PAni as a component of negative electrodes, based on the assumption that PAni is electrically conductive within the working potential range of the anode. However, the mentioned potential range is ~0.0–3.0 V vs. Li/Li^+ (~−3.2 to −0.2 V vs. Ag/AgCl) [2,5,7,9,11], and PAni possesses electrochemical redox activity in the ~3.0–4.2 V vs. Li/Li^+ (~−0.2 to 1.0 V vs. Ag/AgCl) [40–42]. Furthermore, it is known that in aqueous media, PAni loses its conductivity below the potential of about 3.2 V vs. Li/Li^+ (~0.0 V vs. Ag/AgCl) [41,43–45], and the data on the dependence of the electrical conductivity on the potential for PAni in aprotic organic electrolytes commonly used in LIBs are virtually absent [46].

Taking this into account, in this paper we studied electrical and electrochemical characteristics of PAni in a wide range of potentials in an organic electrolyte—a solution of $LiClO_4$ in ethylene carbonate/dimethyl carbonate mixture, which is often used in studies of the electrode materials for LIBs in half-cells with lithium electrodes. Particular attention is paid to dependence of PAni resistance, as well as its redox activity and the value of the specific capacity of the electrode based thereon on various potential ranges during charge-discharge cycling.

---

* Corresponding author. Fax: +380 44 5256672.
E-mail addresses: posol@inphyschem-nas.kiev.ua, oleg.posudievsky@gmail.com (O.Y. Posudievsky).

http://dx.doi.org/10.1016/j.electacta.2015.10.058

Table 1
Application of PAni in anodes of LIBs [28–39].

Anode materials	PAni type	Potential range, V vs Li/Li$^+$	PAni function	Ref.
NanoSn-PAni	PAni·$LiPF_6$	0.0–1.5	Conducting binder	[28]
NiO/PAni film	PAni·H_2SO_4	0.02–3.0	Conducting binder	[29]
Graphene/PAni	PAni·HCl	0.01–3.0	Improvement of electrode conductivity, blocking of SEI formation, electrochemical activity	[30]
SnO_2–PAni/reduced graphene oxide	PAni·HCl PAni·H_2SO_4	0.001–3.0	Conductivity, redox activity (additional capacity), conducting binder	[31]
PAni/TiO_2	Undoped PAni	1.0–2.5	Improvement of lithium ion intercalation inside anatase due to lithium salt doping of the polymer, conducting binder	[32]
PAni–TiO_2–Reduced graphene oxide	PAni·HCl PAni·H_2SO_4	0.01–2.5	Conducting binder, increase of electrode porosity and improvement of lithium ions access to the active component	[33]
MoS_2/PAni	PAni·HCl PAni·H_2SO_4	0.01–3.0	Conducting binder, increase of electrode porosity and improvement of lithium ions access to the active component	[34]
FeS_2/PAni	PAni·H_2SO_4	1.1–2.8	Conducting binder, increase of electrode porosity and improvement of lithium ions access to the active component	[35]
Fe_2O_3@PAni	PAni·HCl PAni·H_2SO_4	0.05–3.0	Conducting binder, increase of electrode porosity and improvement of lithium ions access to the active component	[36]
Zn_2SnO_4/PAni	PAni·HCl	0.01–2.0	Conducting binder, increase of electrode porosity and improvement of lithium ions access to the active component	[37]
Si/PAni	PAni·Phytic acid	0.01–1.0	Improvement of electron and ion conductivity	[38]
Si/PAni	PAni·HCl PAni·H_2SO_4	0.05–1.5	Conducting binder	[39]

2. Experimental

2.1. Reagents

Aniline hydrochloride, hydrochloric and perchloric acids, ammonium hydroxide and ammonium persulfate, were of analytical grade. Lithium metal (99.9%), anhydrous lithium perchlorate (battery grade, 99.99%), ethylene carbonate (99%) (EC), dimethyl carbonate (99 + %) (DMC), *N*-methyl-2-pyrrolidone(99.5%) (NMP) and polyvinylidenefluoride from Aldrich were used for fabrication of the lithium cells. Organic solvents (EC, DMC, NMP) were additionally purified by distillation directly before use.

2.2. Preparation of PAni samples

Samples of PAni necessary for electrochemical studies were prepared by the known method: the reaction between aniline and ammonium persulfate (mole ratio 1:0.8) was carried out in 1 M solution of hydrochloric acid at a temperature of 0–5 °C for 3 h [47]. The residue was separated by filtration, washed and dedoped in 3% aqueous solution of ammonium hydroxide. The prepared PAni in the emeraldine base state was separated by filtration, washed and dried in vacuum at 60 °C.

The samples of PAni doped with $HClO_4$ (PAni·$HClO_4$) were prepared by doping the emeraldine base in aqueous 0.1 M $HClO_4$ for 3 h; PAni·$HClO_4$ was isolated on a filter and dried in vacuum at 60 °C. We used $HClO_4$ for *p*-doping of PAni because a solution of $LiClO_4$ in an ethylene carbonate/dimethyl carbonate mixture was selected as the electrolyte during the electrochemical studies and we did want to add to the electrochemical system other anions (Cl^- or $SO_4{}^{2-}$, for example) to avoid the formation of the insoluble lithium salts.

2.3. Characterization

Measurement of the PAni film resistance (R_f) was carried out in-situ by the method proposed in [46]. To prepare the corresponding sample, emeraldine base was dissolved in NMP, deposited between the two gold microelectrodes and dried in vacuum at 80 °C; then the film was subjected to doping in 0.1 M $HClO_4$ for 3 hours and dried in vacuum at 60 °C.

Cyclic voltammograms (CVA) were recorded using μAUTOLABIII/FRA2 (ECO CHEMIE) in a three-electrode cell with a lithium plate as the counter electrode and a lithium wire as the reference electrode (−3.05 V vs. SHE). The potential scan rate was 0.1 mV/s.

Changes of specific capacity during charge-discharge cycling were studied in Swagelock cells, assembled in a dry glove box filled with argon. Formation of the cathode mass with the composition (unless otherwise stated) PAni:binder = 90:10 was formed under a pressure of 300 atm. Polyvinylidene fluoride was used as the polymer binder. Cathode pellets were pressed onto a stainless steel mesh and dried in vacuum at 80 °C for 12 h. The counter electrode, which was also used as the reference electrode, was fabricated by press-fitting lithium foil to a stainless steel mesh welded to the current collector. The electrodes were separated by a polypropylene separator impregnated with electrolyte. 1 M solution of $LiClO_4$ in an EC/DMC mixture (1:1, vol.%) served as the electrolyte. The water content in the electrolyte was below 7 ppm.

For studies by IR spectroscopy, emeraldine base film was deposited on a stainless steel substrate, cycled in 2.0–4.2 V vs. Li/Li$^+$ potential range to achieve its stable capacity, and then the potential range was changed to 0.05–3.0 V vs. Li/Li$^+$ and charge-discharge cycling was carried out for 20 cycles. Thereafter the polymer electrode was thoroughly washed with DMC, dried in vacuum at 80 °C and separated from the metal substrate. IR spectra were recorded in KBr tablets using SPECTRUM ONE (PerkinElmer) spectrometer with a resolution of 2 cm^{-1}.

3. Results and discussion

It is mentioned above that it is important to study the dependence of PAni resistance on the potential in a wide potential range 0.05–4.2 V vs. Li/Li$^+$ which covers both the range of PAni redox activity [40–42] and the working range of the negative electrodes of LIBs [2,5,7,9,11], since the use of PAni in the electrode materials of LIBs had been based on its electric conductivity. We have conducted such research using the PAni·$HClO_4$ sample, because samples of PAni doped with different Brønsted acids are generally used in the literature (Table 1); the obtained results are shown in Fig. 1.