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Original Research

Electrochemical capacity fading of polyaniline electrode in supercapacitor: An XPS analysis☆

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ABSTRACT

To understand the electrochemical capacity fading of the polyaniline (PANI) electrodes in supercapacitors, for the first time, their chemical structure change during electrochemical cycles was traced with XPS analysis after the HCl doped PANI electrodes were subjected to the cyclic voltammetry test in 1.0 M H_2SO_4 electrolyte for different cycle numbers. The results showed that the chlorine disappeared in the electrode surface, while the surface element contents of sulfur and oxygen increased with the electrochemical cycles increased. It demonstrated that the hydrolytic degradation of the PANI chains and exchange of dopant occurred during the electrochemical cycling, causing the fading in the mechanical and electrochemical performance of the PANI electrodes. This understanding should lead to better design of the conductive polymer-based energy storage devices.

1. Introduction

Conducting polymers are unique kind of photoelectric functional materials possessing highly π-conjugation and reversible doping-dedoping process. Thus they show higher energy density and low-cost, as electrode materials for supercapacitors [1]. The pseudocapacitance based on the conducting polymers originates from the reversible redox reaction of their π-conjugated polymer backbones [2], which is also related to the dopant used as well as the doping mechanism. However, the low mechanical stability and cyclic life of the PANI electrodes restrict their practical application [3], due to the volume expansion and shrinkage of PANI, resulted from the intercalation-deintercalation process of the electrolyte ions during the charge-discharge cycles [4], where the ion exchange of dopant with electrolyte would arise simultaneously [5].

In the present work, the strong evidence of the structure change in the PANI electrodes during the electrochemical cycles has been provided for the first time with XPS analysis technique after subjecting to the cyclic voltammetry (CV) test for different cycles. The PANI electrode was prepared with a dip-coating method using the PANI synthesized with the rapid-mixing polymerization. The results showed that the surface C/O ratio decreased with the increasing of CV cycles and the oxygen content also increased. Additionally, the chlorine content decreased while the sulfur content increased, which might be due to the exchange of electrolyte ion and dopant anion. Therefore, the degradation of the PANI chains and exchange of dopant would arise during the electrochemical cycling, resulting in the degradation of mechanical and electrochemical performance.

2. Experimental

Aniline (Tianjin Chemical Reagent Co. Ltd., Tianjin, China) was freshly distilled under reduced pressure prior to use. $FeCl_3{\cdot}6H_2O$ (analytical reagent grade, Tianjin Chemical Reagent Co. Ltd., Tianjin, China) was used as an oxidant as received. All other reagents were analytical reagents and used without further purification. Doubly deionized water was used throughout.

The PANI was synthesized by the rapid-mixing chemical oxidative polymerization as reported previously [5]: 0.584 mL of aniline and 1.7288 g of $FeCl_3$ were dissolved in 20 mL of 1 M HCl aqueous solution, respectively. Then, the above two solutions were mixed together rapidly within 30 s, after which the mixture solution was kept at 25 °C for 24 h. Finally, the product was washed with 1 M HCl solution and ethanol for several times.

The obtained product, HCl doped PANI, was deprotonated in 100 mL of 1 M ammonium hydroxide for 2 h [6], and then the dedoped PANI was washed with deionized water until neutral to yield the corresponding PANI base. Next, the product was dried at 45 °C for 24 h.

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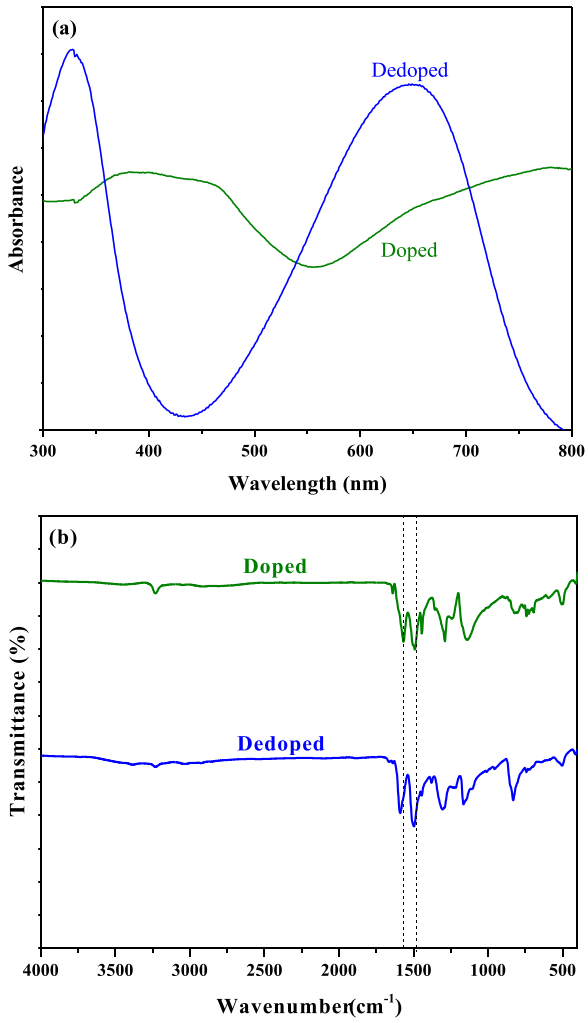

Fig. 1. UV–vis (a) and FT-IR (b) spectra of the doped and dedoped PANI.

Table 1
The capacitance retentions and surface element contents of the PANI electrodes after 0, 100 and 500 cycles by CV test with a scan rate of 100 mV/s.

		0 cycle	100 cycles	500 cycles
Capacitance retention (%)		100	71	60
Surface element content (%)	C1s	73.38	68.30	57.38
	O1s	17.98	18.52	25.35
	N1s	2.90	6.69	7.81
	Cl2p	0.36	0.00	0.00
	S2p	2.32	3.03	5.82
	Si2p	2.50	3.46	3.65
C/O		4.08	3.68	2.26

The PANI electrodes were fabricated by the dip-coating method [7]. Firstly, 0.02 g of the dedoped PANI was dissolved in 2 mL of 1-methyl-2-pyrrolidinone (NMP). Secondly, the one end of the steel mesh (0.5 cm×3 cm) was dipped into the above solution with a coating area of about 0.25 cm^2, after that the electrode was dried at room temperature and this process was repeated for ten times. Thirdly, the electrode was dried at 50 °C for two days, and then the PANI electrode

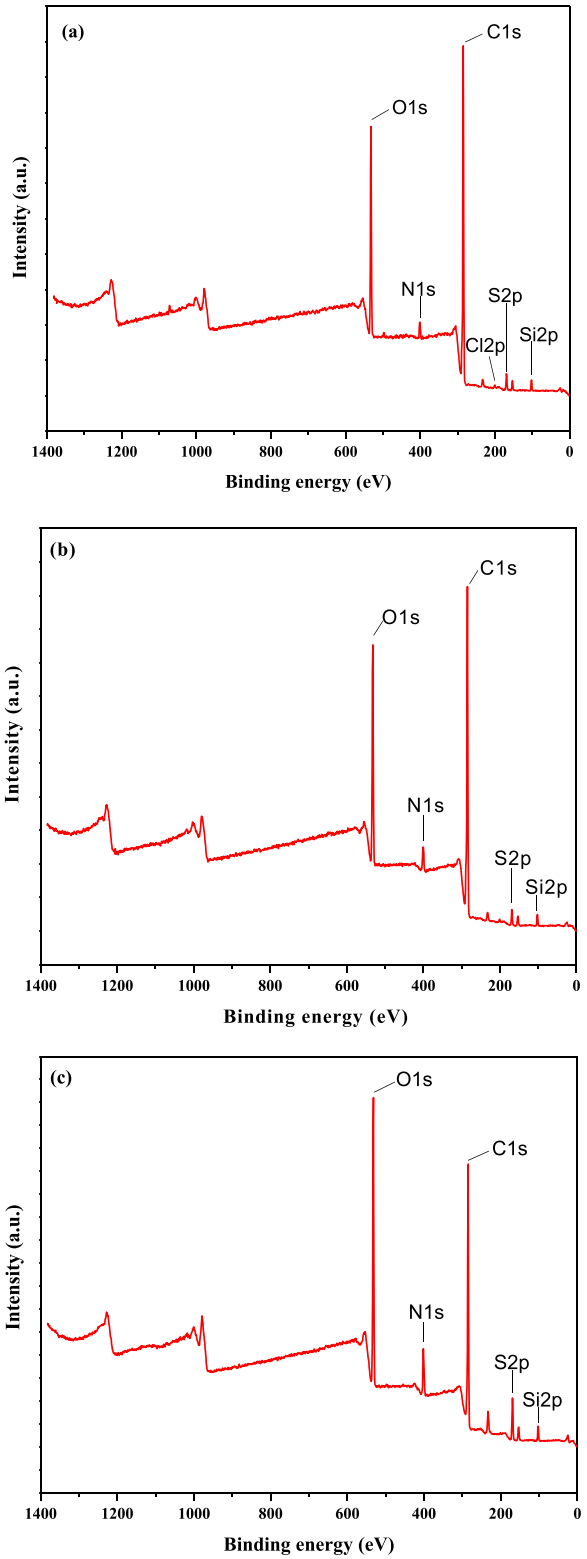

Fig. 2. XPS wide scan spectra of the PANI electrodes after (a) 0, (b) 100 and (c) 500 cycles.

was re-doped with HCl by being immersed into 1 M HCl solution for 1 h. Finally, the electrode was washed with deionized water to remove the surface adsorbed ions, and dried at room temperature.