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H_2 sorption in HCl-treated polyaniline and polypyrrole

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Abstract

Hydrogen sorption in conducting polymers was investigated in order to determine their potential as hydrogen storage media. The conducting polymers, polyaniline and polypyrrole, were treated with an acid, which resulted in an exceptionally high hydrogen sorption, 6 and 8 wt% at room temperature and under 9.3 MPa. Both the molecular effect and electrical effects by the conducting polymers appear to play an important role in hydrogen sorption. This paper presents the preliminary results of hydrogen sorption in a conducting polymer along with its characterization by XRD, scanning electron microscopy, TGA, and conductivity measurement using a four-probe method. A possible mechanism for the extraordinarily high hydrogen storage is suggested.

Keywords: Hydrogen storage; Conducting polymer; Polyaniline; Polypyrrole

1. Introduction

Hydrogen has been attracted considerable attention as a future clean fuel for mobile and stationary purposes. Of the hydrogen life cycle, there has been significant research into hydrogen storage using safe and efficient retrieval methods. Various hydrogen storage media have been investigated [1–4], including carbon nanotubes (CNT), carbon nanofibers, metallic hydrides, metal alloys and glass microspheres.

Recent advances in the hydrogen storage technology by CNT, either single-walled (SWNT) and multi-walled (MWNT) have been made since the Dillon et al. first reported significant H_2 adsorption of as prepared soot containing a trace amount of SWNT, 0.1–0.2 wt% at 133 K [2]. Chen et al. reported an unusually high level of hydrogen adsorption on alkali-doped CNT, 14–20 wt% [5]. Most recently, alkali-doped CNT were found to adsorb only 2 wt% dry hydrogen at room temperature [6]. Liu et al. also reported a high level of hydrogen storage in CNT containing 50–60% SWNT, up to 4.2 wt% if the SWNT had been treated with acid cleaning and subsequent vacuum treatment at 773 K [7]. However, the cost of CNT production and the low hydrogen storage capacity are obstacles to their the practical applications.

Previous studies into CNT-SWNT and B- or N-containing CNT suggests that the tubes have many different structures, which will exhibit either metal or semiconducting properties [8–11]. It is speculated that the metallic characteristics of SWNT, which is induced possibly with the tangling p orbitals of carbon can enhance the level of hydrogen adsorption. Organic materials with similar metallic properties might also be candidates for hydrogen storage media if there is sufficient metallic character present allowing it can adsorb hydrogen in a similar manner to a noble metal.

Conducting polymer membranes have been investigated for the separation of binary gas mixtures such as H_2/N_2, O_2/N_2, CO_2/CH_4, etc. [12–14]. The selectivity and permeability can be tailored by creating a permanent morphology in the conjugated polymer system with repetitive doping, undoping and subsequent redoping. The high selectivity for H_2/N_2 (3590) through the freestanding films of the conjugated polymer, polyaniline, has been reported [12]. The molecular sieving mechanism was proposed for the unusually high selectivity of hydrogen in H_2/N_2. The doping, undoping and redoping treatment generated small micropores, 0.35 nm in diameter,

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which decreased the permeability of larger gases. In addition, the conductivity of the polymer has been suggested to play an indirect role in enhancing the selectivity [15].

The unique permanent morphological structure of the polymer by the doping–undoping–redoping process is expected to allow substantial hydrogen storage. This study examined two conducting polymers, polyaniline (PANI) and polypyrrole (Ppy), as potential hydrogen storage media.

2. Experimental

2.1. Sample preparation

The PANI and Ppy were purchased from Aldrich. Both are inherently conductive polymers after a proprietary doping of organic sulfonic acid. The Ppy was coated on polyurethane core resin with a polymer/urethane core resin ratio of four. For the acid treatment, 500 mg of the conducting polymer was slurred in 15 ml hydrochloric acid (Aldrich, 37%) at room temperature for 24 h. The polymer was then filtered, washed thoroughly with deionized water and dried in oven at 360 K for 24 h to eliminate the adsorbed water. The fine powder was made into a 13 mm diameter self-supporting wafer using an IR press with a pressure of 3000 kg cm^{-2}. The pellet is more stable in ambient air than the powder [16]. The pellet was again crushed into 1–2 mm particles in order to measure the level of hydrogen storage.

2.2. Measurement of hydrogen sorption

The hydrogen sorption capacity of the polymer was measured using an automatic Sievert's type *PCT* measurement apparatus that is similar to that reported by Liu et al. [7]. A control experiment was carried out to measure the pressure change at 298 K over a 1 h period using an empty sample cell, which was immersed in water during the measurements in order to detect the leakage through the connection, evacuated and then charged with 9.3 MPa ultra high purity hydrogen (99.999%) until the pressure reached 10^{-3} Torr. The level of hydrogen storage of ~100–500 mg of the polymer weighing was performed for 1 h using the same process. The hydrogen sorption capacity of the polymer based on the pressure changes was calibrated with the control data. Between the measurements, the cell containing the polymer was heated to 473 K to completely remove the adsorbed gas. The hydrogen adsorption measurements were begun when the pressure reached 10^{-3} Torr after cooling the sample to room temperature. The level of hydrogen storage of the known reference materials such as metallic hydrides was measured using the same apparatus.

3. Results and discussion

The level of hydrogen sorption on the Ppy and the PANI was measured after evacuation at 298 K to 10^{-3} Torr, as shown in Fig. 1. The level of hydrogen sorption on the PANI occurred progressively for 1 h, initially reaching ~3.5 wt% hydrogen sorption. The sample was evacuated again to remove the adsorbed hydrogen at 298 K. The second sorption of hydrogen on the PANI gave a small level of hydrogen adsorption, ~1.6 wt%. This sequential sorption on the PANI suggested possible reversible adsorption about 45% like hydrogen sorption in novel metal catalyst. The sample was then evacuated at 473 K to remove the adsorbed hydrogen. The level of sorption increased to ~6.4 wt%. Such a large increase in the hydrogen sorption might be due to the desorption of impurities, which had been removed completely through evacuation at 473 K.

However, the equilibrium level of hydrogen sorption was not reached even for a 1 h equilibrium time. Liu et al. reported that a much longer equilibrium time, typically 6 h, is needed [7]. The longer adsorption time suggests Knudsen diffusion of the hydrogen into the molecular scale pores, which is similar to that proposed for the gas separation of polymer membranes [17].

The Ppy sample also showed a significant amount of hydrogen sorption, 1.6–2.7 wt%. The Ppy sample was coated

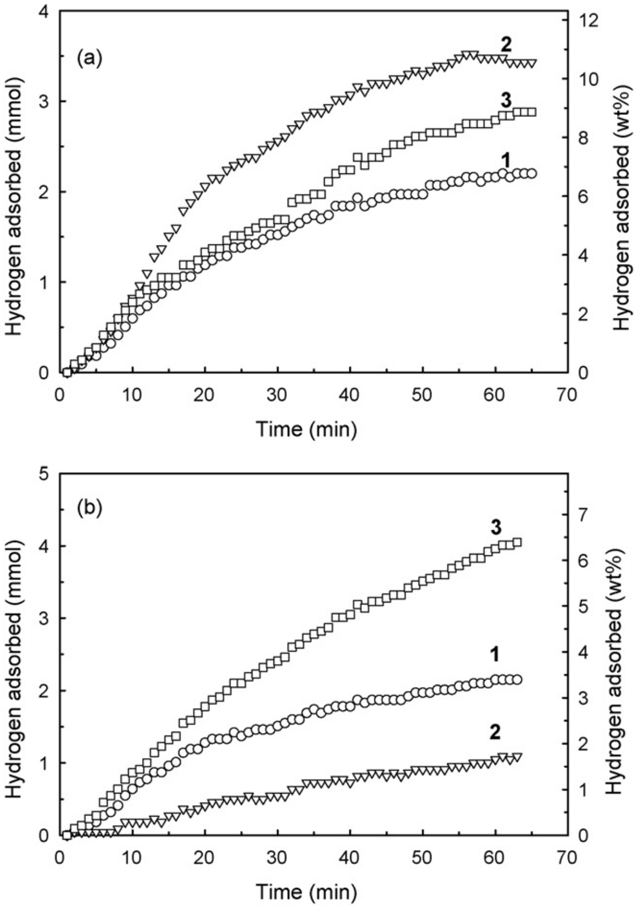

Fig. 1. The level of H_2 in wt% for both (a) the Ppy and (b) the PANI treated with HCl. (a) 1 indicates the first adsorption of hydrogen at 298 K, and 2 and 3 indicate the second and the third adsorption measurements after the heating the polymer to 473 K under a vacuum with subsequent cooling to room temperature. (b) The same treatment was applied to 1 and 3, the first and the third adsorption measurements as that of the Ppy. However, with 2 in (b), for the second measurement was carried out after evacuation at room temperature until the pressure reached 10^{-3} Torr. The sample weights of the PANI and the Ppy used for the hydrogen adsorption measurements were 127 and 260 mg (65 mg pure Ppy), respectively.

on polyurethane core resin with a polymer/urethane core resin ratio of 4. Hence, hydrogen sorption on the Ppy sample could be obtained by multiplying the experimental value by four since the polyurethane shows a negligible hydrogen sorption. The amount of hydrogen sorption depended on the thermal treatment, as shown in Fig. 1(b). A conducting polymer can degradable thermally. Such thermal stability of the Ppy might result in the differences in the level of hydrogen sorption when the sample is heated to 473 K repeatedly in order to remove the adsorbed hydrogen.

Fig. 2 shows the weight change in the HCl treated sample depending on the thermal cycle. A significant decrease in weight was observed in the first heating cycle, approximately 3 and 6 wt% for the HCl-treated PANI and Ppy polymers, respectively. The large decrease in weight during the first cycle was attributed to adsorbed impurities and water. After the first thermal cycle, the decrease in weight reduced to approximately 0.5 wt% for both samples, which was due to thermal degradation of the conducting polymer. This suggests that the thermal stability of the conducting could be an obstacle for the hydrogen sorption–desorption cycle.

Table 1 shows the hydrogen sorption in the metal hydrides and MWNT for comparison. The level of hydrogen sorption in the metal hydrides was slightly lower than the reported value for both AB_5 and AB_2 types [18,19]. The level of hydrogen storage in the MWNT [20] prepared at 800–1100 K using a catalytic method with a Ni catalyst and methane as the carbon source was only 0.8 wt% under similar conditions. The level of hydrogen sorption in the acid-treated polymer was reproducible within ± 1 wt% during a few tens of adsorption/retrieval cycles, in which the desorption of hydrogen was carried out 473 K. This is because only approximately 50% of the hydrogen was removed at room temperature.

Table 1
Summary of the level of hydrogen storage in metal hydrides, multi-walled carbon nanotubes and the acid treated conducting polymer measured using the same adsorption apparatus

Sample	Pressure (atm)/ temperature (K)	wt%
$MmNi_{4.7}Al_{0.3}$	10–20/298	1.2
$MmNi_{4.8}Al_{0.2}$	10–20/298	1.3
$Ti_{0.7}Zr_{0.3}\ Mn_{1.0}Cr_{0.9}Ni_{0.02}Fe_{0.03}$	10–20/298	2.0
MWNT[a,b]	90/298	0.8
HCl-treated PANI[b]	90/298	6.0
HCl-treated Ppy[b]	90/298	8.0

[a] Synthesized from the decomposition of CH_4 at 800–1100 K over catalysts such as Ni/MgO and Ni/USY. The purification of the obtained CNT was carried out in order to remove the amorphous carbon by dissolving the sample in a HF solution followed by ultra-sonication.

[b] Exposed to ~90 atm ultra high purity hydrogen (99.999%) for 1 h.

The effect of the HCl treatment on the conducting polymer was observed as a change in the surface structure, as shown in Fig. 3. The concentrated hydrochloric acid treatment of the polymer resulted in the replacement of a large organic dopant molecule (OSA) such as camphor sulfonic acid (CSA) and dodecylbenzene sulfonic acid (DBSA) into the smaller dopant, HCl. Hence, a morphological change in the polymer texture in the self-supporting wafer is observed, as in Fig. 3. The acid treatment of the PANI might induce the formation of micropores or micro-leaks that are desirable for the hydrogen sorption or gas separation [12–14]. The combined analysis of the PANI before and after the acid treatment using EDX measurements and elemental analysis showed that 65% of the total organic sulfonic acid had been replaced with the smaller Cl^- dopant while the total dopant level was maintained at $PANI(OSA)_{0.45}$ and $PANI(OSA)_{0.16}(HCl)_{0.29}$ before and after the acid treatment, respectively (Fig. 4). The molecular scale micropores appear to be generated due to the exchange of the larger dopant molecules, CSA or DBSA, into smaller ones if the structure of the polymer backbone is to maintain sufficient rigidity. There was no hydrogen sorption over the conducting polymer without the acid treatment. However, KA zeolite with small micropores, 0.3 nm, was reported to have a hydrogen storage capacity of 9.2 $cm^3\ g^{-1}$, which is too low to compete with metal hydrides, 150–700 $cm^3\ g^{-1}$ [21]. Therefore, the electronic structure of the polymer also appears to play a significant role in hydrogen sorption.

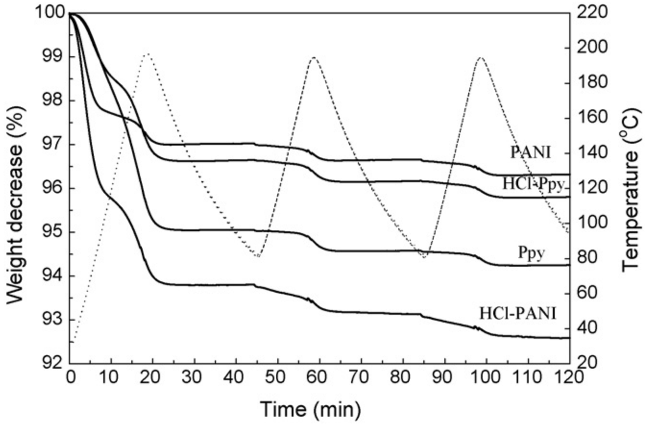

Fig. 2. Thermogravimetric analysis of the conducting polymer during the thermal cycle in nitrogen atmosphere. The dotted line indicates the change in the sample temperature.

The exchange of large organic sulfonic acids with HCl decreased the bulk conductivity from 5 to 0.4 S/cm for PANI, and from 3.1×10^{-3} to 0.9×10^{-3} S/cm for Ppy, respectively. However, the XRD intensity of the PANI at $2\theta = 15–20^\circ$ was increased by the acid treatment, as shown in Fig. 5, which suggests an improvement in crystallinity. The improved crystallinity might increase or impart higher intrinsic metallic properties in the microscopic regions of the polymer but not bulk conductivity, as expected from the characteristics of the dopant and the poor grain boundaries shown in Fig. 3. The conduction process followed a heterogeneous model consisting of ordered crystalline and disordered amorphous regions [22,23]. The conduction process in the ordered crystalline region of the conducting polymer was so rapid that the hoping motion in the disordered amorphous region appears to be a limiting mechanism. Therefore, the achievable conductivity from the PANI-CSA was claimed to higher than that of copper if all the charge carrier density in the localized metallic islands containing delocalized carriers participates in the conduction

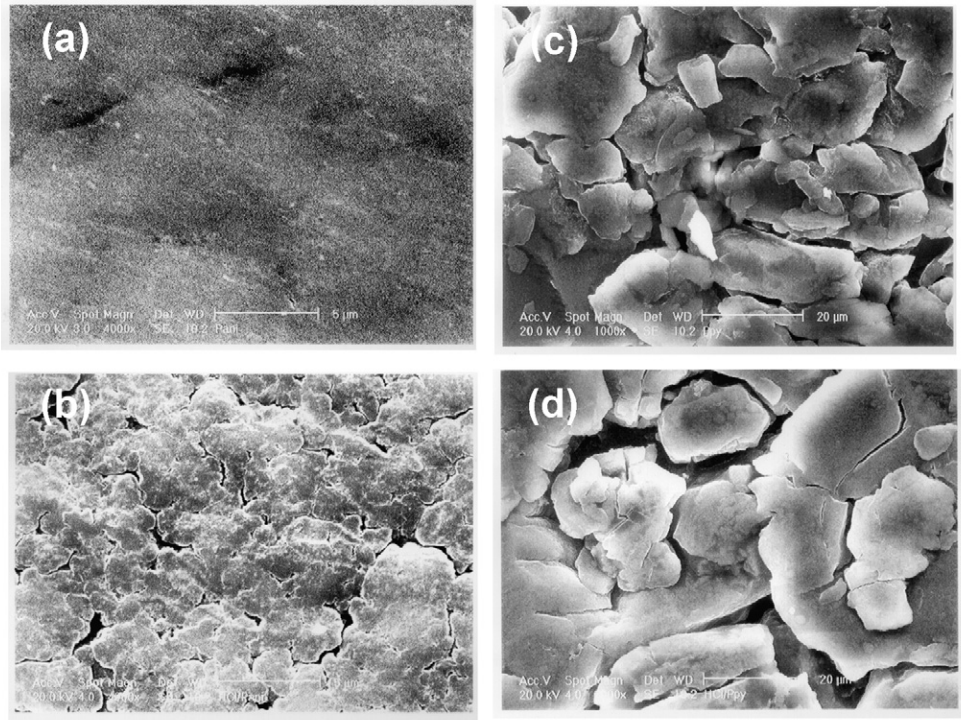

Fig. 3. Scanning electron micrographs of the PANI (a) before and (b) after the HCl treatment and the Ppy (c) before and (d) after the HCl treatment using Philips XL 10 series. The fine polymer powder was made into a 13 mm diameter self-supporting wafer using an IR press with a pressure of 3000 kg cm^{-2}.

process [24]. Hence, the poor conductivity of the HCl-treated PANI and Ppy sample might be due to the poor hopping conditions, as shown in Fig. 3. This suggests that the inherent conductivity can be increased, which is beneficial for hydrogen sorption. On the other hand, the bulk conductivity was estimated to be low in the presence of the micropores. Recently, Panella et al. reported the volumetric measurement of hydrogen storage in HCl-treated polyaniline and polypyrrole

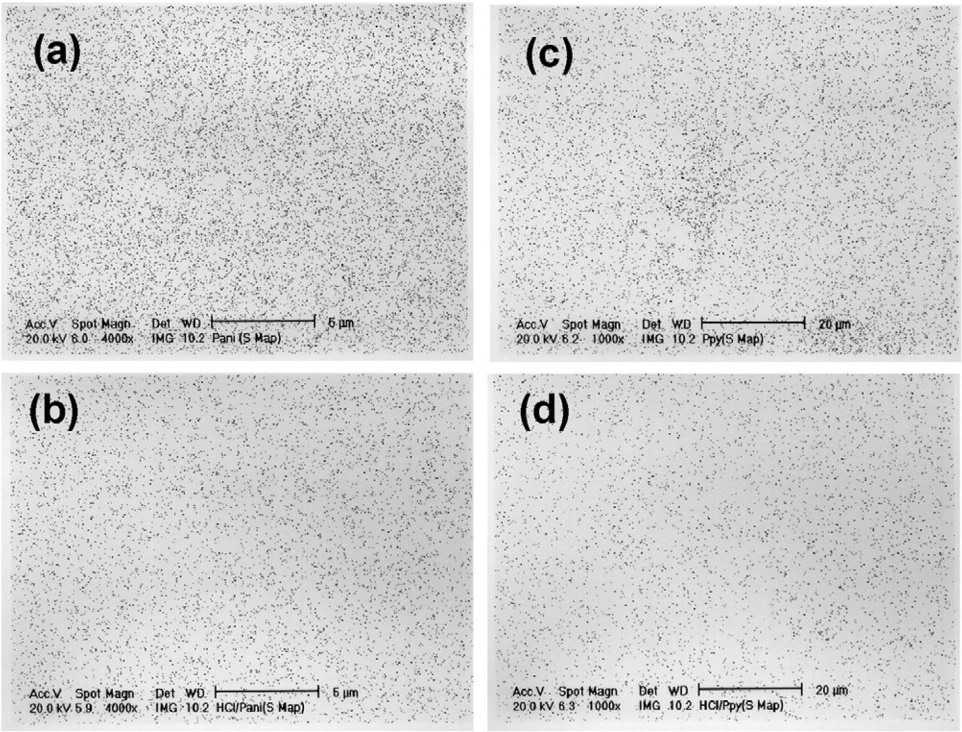

Fig. 4. Mapping of the distribution of the S Kα line in the PANI (a) before and (b) after the HCl treatment and the Ppy (c) before and (d) after the HCl treatment. The dot indicated the sulfur component.

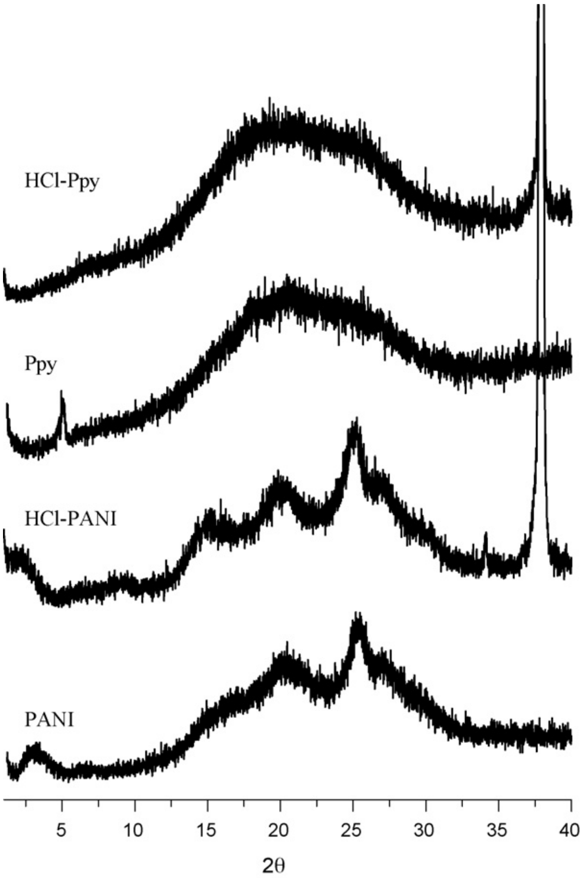

Fig. 5. X-ray diffraction patterns of the conducting polymer before and after the HCl treatment.

following the similar preparation procedure [25]. However, they found there was no hydrogen sorption in the sample, contrary to the present work. This is probably due to the difference in the presence of the micropore in the conducting polymer created during the repetitive doping, undoping and subsequent redoping process [12–15] or the exchange of bulky dopant into smaller one as discussed above. More detailed characterization technique except the BET method using nitrogen at 77 K is necessary to clarify the presence of the micropore in the conducting polymer which is susceptible for the shrinkage at low temperature.

4. Conclusions

The unusual hydrogen adsorption observed in the conducting polymers is believed to be the result of the combined effect of the molecular sieving and the conjugated conducting electronic environment in which hydrogen can be stabilized, presumably due to the metallic character of the conduction band. However, more theoretical and experimental studies on conducting polymers as a new class of hydrogen storage media will be needed before they are proved to be safe and inexpensive adsorption/retrieval systems.

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References

[1] E. Ewald, Int. J. Hydr. Energy 23 (1998) 803–814.
[2] A. Chambers, C. Park, R.T. Baker, N.M. Rodriguez, J. Phys. Chem. B 102 (1998) 4253–4256.
[3] A.C. Dillon, et al. Nature 386 (1997) 377–379.
[4] H. Buchner, et al., Hydrogen and Other Alternative Fuels for Air and Ground Transportation, Wiley, Chichester, UK, 1995.
[5] P. Chen, X. Wu, J. Lin, K.L. Tan, Science 285 (1999) 91–93.
[6] R.T. Yang, Carbon 38 (2000) 623–626.
[7] C. Liu, et al. Science 285 (1999) 1127–1129.
[8] T.W. Odom, et al. Nature 391 (1998) 62–64.
[9] W.K. Hsu, et al. Chem. Phys. Lett. 323 (2000) 472–479.
[10] Y. Huang, J. Gao, R. Liu, Synth. Met. 113 (2000) 251–255.
[11] X.-P. Tang, et al. Science 288 (2000) 492–494.
[12] M.R. Anderson, B.R. Mattes, H. Reiss, R.B. Kaner, Science 252 (1991) 1412.
[13] R.B. Kaner, Nature 352 (1991) 23.
[14] D. Gulsen, P. Hacarloglu, L. Toppare, L. Yilmaz, J. Membr. Sci. 182 (2001) 29–39.
[15] H. Reiss, in: W.R. Salaneck, I. Lundström, B. Rånby (Eds.), Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure, Oxford University Press, New York, 1993, pp. 263–272.
[16] P. Rannou, M. Nechtschein, Synth. Met. 82 (1997) 755–756.
[17] G. Illing, K. Hellgardt, R.J. Wakeman, A. Jungbauer, J. Membr. Sci. 184 (2001) 69–78.
[18] G. Liang, J. Huot, R. Schulz, J. Alloys Compd. 320 (2001) 133–139.
[19] F.-J. Liu, S. Suda, G. Sandrock, J. Alloys Compd. 232 (1996) 232–237.
[20] H.M. Cheng, Q.H. Yang, C. Liu, Carbon 39 (2001) 1447–1454.
[21] J. Weitkamp, M. Fritz, S. Ernst, Int. J. Hydr. Energy 20 (1995) 967–970.
[22] J. Joo, et al. Phys. Rev. B 57 (1998) 9567–9580.
[23] B. Beau, J.P. Travers, E. Banka, Synth. Met. 101 (1999) 772–775.
[24] J. Joo, A.J. Epstein, V.N. Prigodin, Y. Min, A.G. MacDiarmid, Phys. Rev. B: Rapid Commun. 50 (1994) 12226–12229.
[25] B. Panella, L. Kossykh, U. Dettlaff-Weglikowska, M. Hirscher, G. Zerbi, S. Roth, Synth. Met. 151 (2005) 208–210.