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# Polyaniline Nanofibers Obtained by Electrospin Process for Hydrogen Storage Applications

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## Abstract

Conducting polymer nanostructures combine the advantages of organic conductors and low dimensional systems and therefore should yield many interesting physicochemical properties and useful applications. This leads to much faster and more responsive chemical sensors, new organic / polyaniline nanocomposites and ultra-fast non volatile memory devices. In conventional polymerization, nanofibers are subject to secondary growth of irregularly shaped particles, which leads to the final granular agglomerates. The key to producing pure nanofibers is to suppress secondary growth. Based on this, two methods – interfacial polymerization and rapidly mixed reactions have been developed that can readily produce pure nanofibers by slightly modifying the conventional chemical synthesis of polyaniline without the need for any template or structural directing material. With this nanofiber morphology, dispersibility and processbility of polyaniline are now much improved. In the present investigation, highly rough and large surface area polyaniline nanofibers have been grown by using a electrospinning process already synthesized polyaniline using polymethylmethacrylate (PMMA) as polymer binder. Several experiments have been carried out under different parameters such as distance between the substrate and syringe, different wt% load of PMMA in PANI, voltage applied between substrate and syringe in order to obtain nanofibers as thin as 60 nm in diameter. Structural, Morphological, Structural, Chemical, optical properties have been investigated. Effect of surfactants and polymer binder on the formation of polyaniline nanofibers morphology, structure has been systematically investigated. We also have carried out the investigation to reversibly store $H_2$ in these polyaniline nanofibers. The rate of hydrogen sorption during the initial run is found to be very rapid and an extended plateau pressure of about 30 bars is obtained from the pressure-composition isotherm profiles of these polyaniline nanofibers. The reversible cycling capacity of ~10.5 wt.% is demonstrated at an operating temperature of 120C and have been attributed due their unique microstructural and surface properties.

**Keywords**: hydrogen storage nanomaterials, polyaniline-poly vinyl pyrrolidene, electrospinning, wet chemical, conducting polymer

## 1. Introduction

The hydrogen storage problem is one of the major issues that needs to be resolved if hydrogen is to become a viable energy carrier in the future. An earlier EUR report examined the problem, including its possible solution through the use of a solid state storage material. This option is one of the most attractive for a number of reasons, although no material currently satisfies the practical requirements, in terms of storage capacity, operating temperature and pressure ranges, impurity resistance, long term cycling stability and cost. The search for a material that fulfils the criteria for a practical store is therefore generating a great deal of scientific research interest, and an increasing number of publications on this topic are appearing in the scientific literature. A crucial part of the search for new storage materials is the accurate determination of the hydrogen sorption or storage characteristics of new or modified materials. This is an issue that has come to prominence in recent years due to the controversy over the potential storage capacity of carbon nanostructures, such as nanotubes and nanofibres, during which widely varying claims of potential storage capacity and hydrogen uptake behavior were made. A significant contribution to this controversy was made by inaccuracy in the measurement of the potential gas phase hydrogen storage capacities of these nanostructured carbon materials.

The problem of storing hydrogen safely and effectively is one of the major technological barriers currently preventing the widespread adoption of hydrogen as an energy carrier and the subsequent transition to a so-called "hydrogen economy". Practical problems with the storage of hydrogen in both gaseous and liquid form appear to make solid state storage the most attractive proposed solution, and so the search for potential solid state hydrogen storage media is attracting a significant amount of research interest from both academia and industry. Various types of materials have been proposed and are currently being investigated, including microporous materials that can store physisorbed molecular hydrogen at low temperatures, intermetallic hydrides that absorb atomic hydrogen as an interstitial and complex hydrides formed from light elements, such as Li, B, Na, Mg and Al.

The search for potential hydrogen storage materials has recently been receiving a great deal of attention, as the hydrogen storage problem is one of the major issues that needs to be resolved if hydrogen is to become a viable energy carrier in the future [1-

3]. The search for new materials and the various proposed solutions to the problem have both been covered in a number of recent review articles [3-11]. Aside from the so called ‘chemical hydrides’ [12], the materials currently being considered can be broadly separated into two categories: one in which the hydrogen is absorbed in the bulk of the material in atomic form and the second in which the hydrogen is weakly bonded in molecular form to the surface of the material. The former is hydrogen *ab*sorption and the latter hydrogen *ad*sorption. Both of these processes can be measured or monitored using bulk gas phase characterization methods that loosely mimic the process by which a practical solid state hydrogen store would be charged or discharged. Volumetric and gravimetric techniques determine the hydrogen sorption properties of a material by exposing it to a pressure of hydrogen at a given temperature, causing a reaction that results either in the sorption or desorption of hydrogen, depending on whether there has been an increase or decrease in the applied pressure from the previous step. The measured hydrogen content at different hydrogen pressures is then plotted to form an isotherm. Temperature-programmed techniques, on the other hand, use temperature changes to sorb and desorb the hydrogen. An experiment therefore consists of taking the sample from a low temperature, at which hydrogen is thermodynamically or kinetically trapped in the material, to a higher temperature, at which the hydrogen will be partially or fully desorbed, and monitoring the quantity of hydrogen released.

These types of sorption measurements have previously been performed for a number of different reasons. In metal hydride research, the measurement of the absorption of hydrogen by elemental metals and intermetallic compounds has been made for reasons ranging from understanding the fundamental interaction of hydrogen with matter [14-19] to the development of specific technological applications, both gas phase [20], such as metal hydride heat pumps, and electrochemical, such as nickel metal hydride batteries [21-23]. The measurement of gas adsorption on porous materials, meanwhile, is another mature research field in which measurements have been made using similar techniques to those of hydride research but for the purpose of surface area, pore size distribution (PSD) and porosity determination. However, for a number of reasons, hydrogen is not a common probe gas2, and so there is a great deal more literature available on the adsorption of the typical probe gases compared to the adsorption of hydrogen [26]. Although there are many similarities between the methods used for these measurements, there are also issues that are specific to hydrogen sorption and, in particular, to the application of gaseous hydrogen storage.

## 2. Experimental Procedure

Aniline, ammonium persulfate, camphorosulfonic acid are used as received from Sigma-Aldrich. Polyaniline nanofibers (PANI-NF) have been synthesized by oxidative polymerization of aniline monomer at $0^{o}$C in an ice bath using ammonium persulfate as the oxidant in the presence of surfactant. Sulfonic acid based surfactants as the dopant and ammonium persulfate as the oxidant were used in the present synthesis of polyaniline nanofibers. Polyaniline nanofibers were synthesized by oxidative polymerization of aniline monomer at $0^{o}$C in an ice bath using ammonium persulfate as the oxidant in the presence of surfactant. Calculated quantities of aniline monomer (0.05 moles) were mixed with 50 ml of distilled water and stirred using magnetic stirrer for 10 minutes. Meanwhile, calculated quantities of surfactant (0.5 moles) and oxidant (0.05 moles) were dissolved separately in distilled water and stirred for 10 minutes in an ice bath. The Surfactant solution was first added into the aniline monomer aqueous solution and then previously cooled oxidant solution drop wise and the mixture was allowed to react for 15 hours in an ice bath. The precipitate was filtered and washed several times with distilled water and methanol to terminate the polymerization reaction and then dried in vacuum at room temperature for 24 hours. Later, the vacuum-dried precipitate was annealed at $100^{o}$C for 15 hours. The dried polyaniline was mixed with 15 wt% of polyvinyl alcohol polymer as bonder to draw nanofibers using electrospin technique. The obtained nanofibers have been subjected to characterization followed by tested for the hydrogen uptake and release measurements.

### 2a. Electrospinning Process:

Electrospinning is a simple and versatile method to produce polymer nanofibers by accelerating a charged polymer jet in a very high electric field. The diameter of the fibers are in the range of 10µm to 10 nm, which is typically 1-3 orders less than that obtained by the conventional spinning process. The main components of the electrospinning process can be classified as (i) syringe (or pipette), (ii) high voltage power supply and (iii) counter electrode or substrate. Polymer in solution (or melt) form is loaded in the syringe and is connected to the positive terminal (it also can be negative terminal) of the high voltage power supply. For continuous production of nanofibers, the solution should be pushed at a constant flow rate. Generally, a syringe pump serves this purpose.

In this process a high voltage is used to create an electrically charged jet of polymer solution or melt. One electrode is connected to the spinning solution/melt and the other attached to the collector. In most cases, the collector is simply grounded and the electric field is concentrated at the tip of the needle that contains a pendant droplet of the solution held by its surface tension. Accordingly, charges are induced on the surface of the drop. Mutual charge repulsion and the tendency of the surface charges to move towards the counter electrode, result in an electrostatic force against surface tension. As the intensity of the electric field is increased, the hemispherical surface of the fluid at the tip of the capillary tube elongates to form an inverted cone known as the Taylor cone. On increasing the electric field further, a critical value is reached when the repulsive electrostatic forces overcome the surface tension forces and a fine jet of charged polymer solution is ejected from the tip of the cone. This jet is further subjected to elongation process and instabilities, which results in the jet becoming very long and thin as they move towards the counter electrode. The polymer strands now start moving away from each other due to mutual repulsion and ultimately collect on the counter electrode as a random coil of nanofibers. Once the jet comes into the atmosphere, the low boiling point solvent evaporates, leaving behind only the charged polymer strands. Fig 1 depicts the picture of the Electrospin unit in which the nanofibers have been produced.

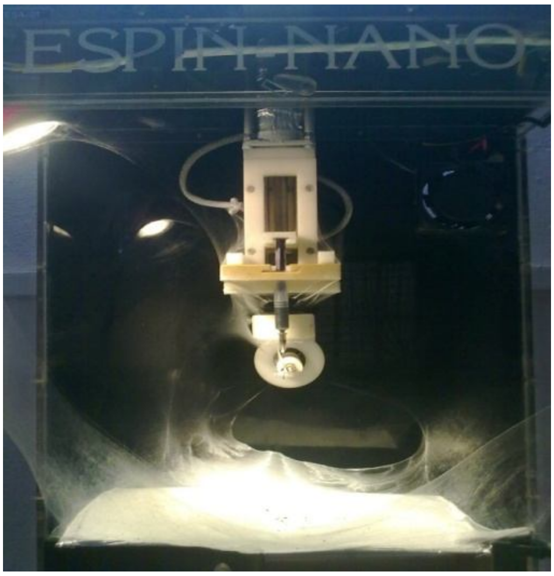
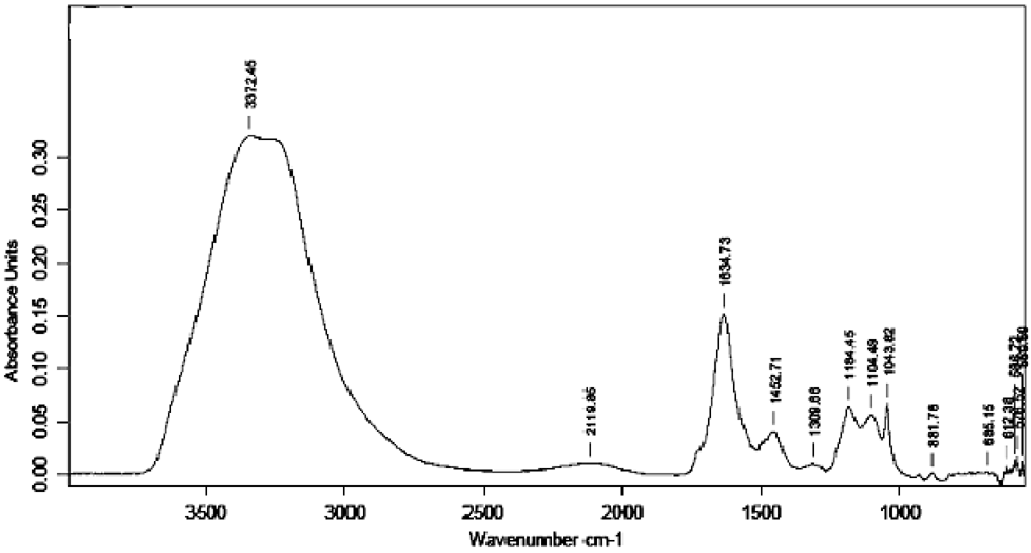


**Figure 1**: Picture of the electrospin apparatus with the nanofibers formed at the bottom collected in a planar sheet.

## 3. Results and Discussion

### 3a. FT-Infrared spectroscopy:

FTIR spectra of PVA and PVA-PANI nanofibers were recorded using FTIR Nicolet 6700 (Thermo Fisher Scientific, Madisson, WI, USA) operated by Omnic software 8.1. In particular, for nanofibers measurement the spectra were obtained by attenuated total reflectance (ATR) method using smart orbit diamond ATR. Briefly, the formulations were placed individually on the sample plate of the smart orbit and screwed lightly to record IR spectra in ATR mode.



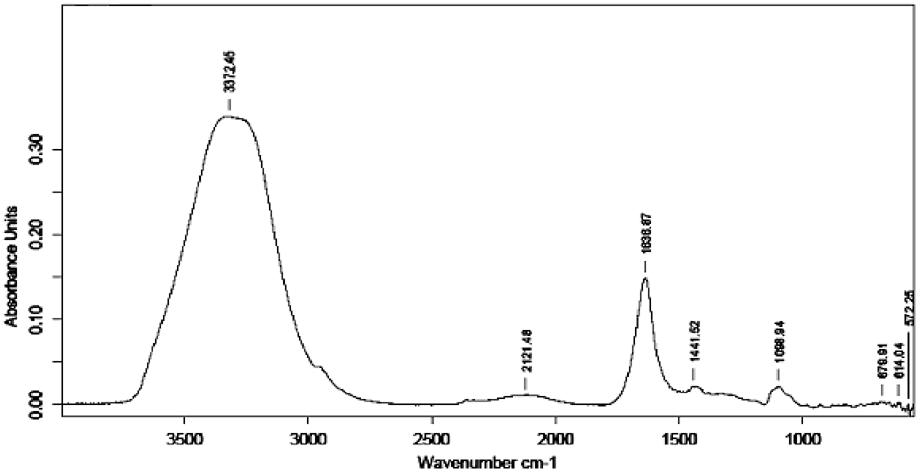


**Figure 2**: FTIR of PVA and PVA-PANI nanofibers grown by Electrospinning Technique at 25$^{o}$C

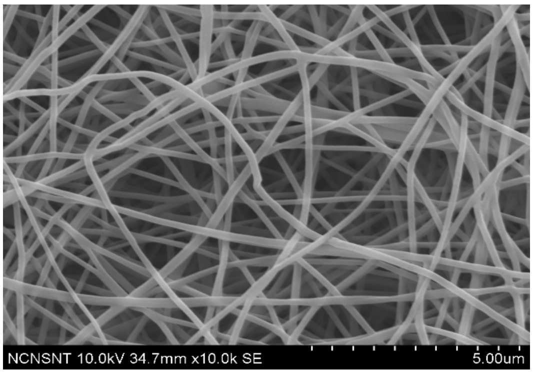
PVA nanofibers have exhibited stretching vibration band of hydrogen-bonded alcohol ( OH) at 3372 cm$^{−1}$. PVA-PANI nanofibers have exhibited stretching vibration band of hydrogen-bonded alcohol ( OH) at 3372 cm$^{−1}$ for PVA conformation and the aromatic C-H bending in the plane (1167cm$^{-1}$) and out of plane (831cm$^{-1}$) for 1,4 disubstituted aromatic ring indicated linear structure of PANI.

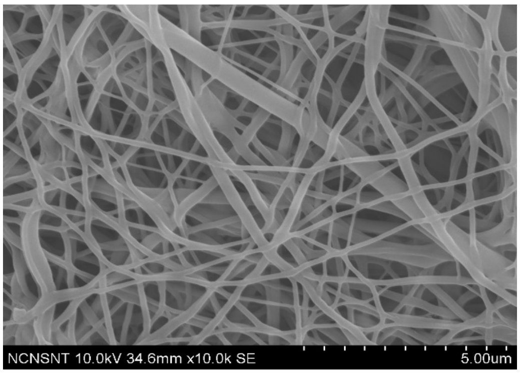
### 3b. FE-Scanning electron spectroscopy:

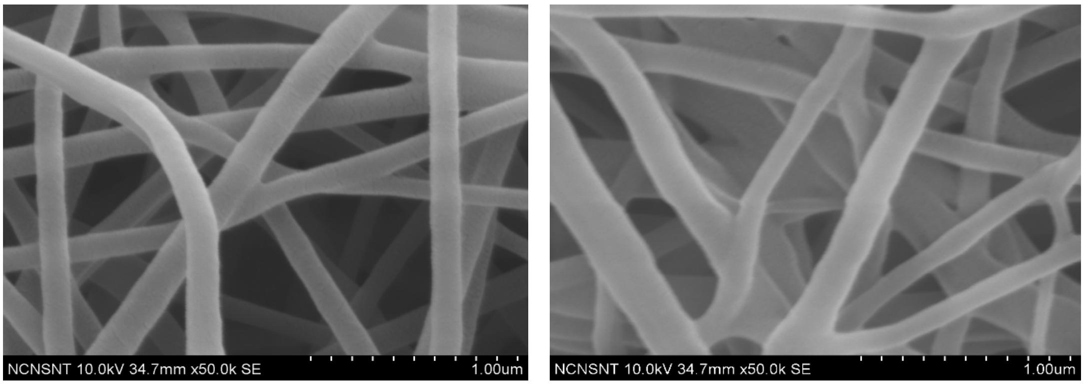
The surface morphology of the pure drug and oral thin films containing drug and polymer were characterized by Field Emission Scanning Electron Microscope (FESEM, FEI Sirion) at operating voltage of 5–30 KV. All images were recorded at working distance of 8-10 mm.

Uniform pure PVA nanofibers with diameter 100 nm have been obtained by electrospin process as shown in Figure 19 (Left -top- high magnification and bottom high magnification)

Fine and uniform PVA-PANI nanofibers with diameter 80-100 nm have been obtained by electrospin process as shown in Figure 3 (top- low magnification and bottom high magnification)







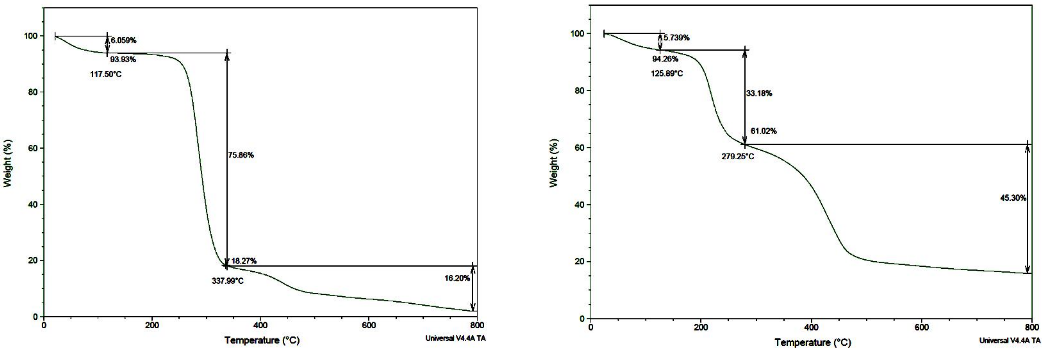
SEM images of PVA nanofibers grown by electrospin technique (a) high magnification (b) low magnification

SEM images of PVA-PANI nanofibers grown by electrospin technique (a) high magnification (b) low magnification

**Figure 3**: PVA nanofibers obtained by electrospin technique at 25kV and 15cm distance.

### 3c. Thermogravimetric analysis:

DSC (Mettler–Toledo DSC 821e, Switzerland) analysis was carried out with initial and final temperatures at 25°C and 300°C with temperature raise of 10°C/min in argon atmosphere. DSC curves were evaluated with STARe software supplied by the Mettler-Toledo company.



TGA of pure PVA nanofibers grown by Electrospin Technique at 25K (15 cm)

TGA of PANI-PVA nanofibers grown by Electrospin Technique at 25K [15cm]

**Figure 4**: Pure PVA-PANI sample has shown water removal at 100°C and decomposition of PVA started at 400°C and completed at 600°C

Pure PVA sample has shown water removal at 100°C and decomposition of PVA started at 337°C and completed at 600°C as shown in Figure 4.

## 4. Hydrogen Sorption Measurements of PANI Fibers Obtained by Electrospining Technique

The volumetric hydrogen sorption measurements (kinetics, PCT, cycle life) are of paramount importance in understanding the hydrogen storage behavior of PANI-NF. Hydrogen absorption at different temperatures (25–100$^{o}$C) was executed at a high pressure (H2w80 bar) with a pre-calibrated reservoir. These isothermal volumetric measurements were carried out by Hy-Energy's PCTP 2000 sorption equipment. This fully automated Sievert's type instrument uses an internal PID controlled pressure regulator with maximum pressure of 170 bars. It also includes five built-in and calibrated reservoir volumes of 4.66, 11.61, 160.11, 1021.30 and 1169.80 mL. The volume calibration with and without the sample was performed at a constant temperature with an accuracy of 1$^{o}$C using helium. The software subroutines for hydrogen purging cycles, leak test, kinetics, PCT and cycling were performed by the HyDataV2.1 Lab-View program. The data collected for each run were analyzed using the Igor Pro 5.03 program with a built-in HyAnalysis Macro.

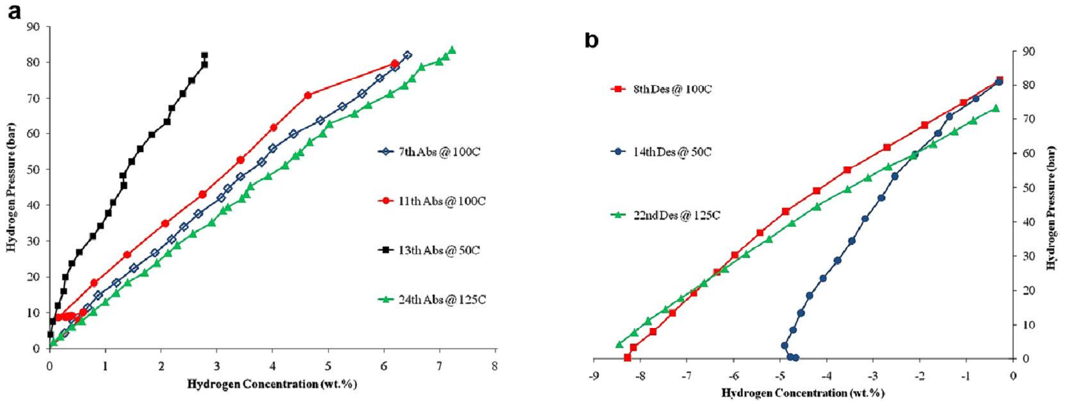


**Fig. 5:** Hydrogen (a) adsorption and (b) desorption PCT curves for the PANI-NF.

The as-synthesized PANI-NF electrospun sample was loaded into a schlenk flask and sealed with a rubber cap for vacuum drying at 125$^{o}$C for 3 h. Thus annealed material was immediately transferred to a high pressure hydrogen reactor under the nitrogen filled glove box. The sealed reactor was connected then to the high hydrogen pressure volumetric set-up to measure the sorption behavior. Pressure-Composition-Temperature (PCT) profiles of the PANI-NF during hydrogen adsorption and desorption were plotted in Fig. 5 (a) and (b).

Hydrogen storage capacity increases with increasing temperature from 50 to 125$^{o}$C in various cycles as shown Fig. 5(a). At lower temperature of 50$^{o}$C, a hydrogen capacity of 3 wt.%, whereas at 100–125$^{o}$C, at least two fold increase of capacity (6–8 wt.%) was invariably obtained at various hydrogenation cycles. At the end of each adsorption PCT, desorption PCT experiments were performed by reducing the hydrogen pressure in steps of 6P ¼ 3 bar, and are depicted in Fig. 5(b). A hydrogen storage capacity of 2–8 wt.% was obtained at temperature range of 50–125°C. Fig. 6(a) represents the hydrogen absorption kinetic curves of the PANI-NF sample after 55 previous sorption cycles at 30°C. It can be seen that after approximately 2 h at 80 bar of $H_2$ pressure close to 5 wt.% of hydrogen is absorbed. From the same figure, the hydrogen desorption was plotted after 66 cycles at 100°C and reveals that the kinetics are rather rapid, with most of the hydrogen being released in less than 30 min for a total hydrogen release of close to 6 wt.%.

Additionally, the absorption kinetics in the 64th cycle of hydrogen at 80 bar pressure with varying temperature is shown in Fig. 6(b). Initially, the hydrogen is absorbed at 125°C with saturation occurring after approximately 2 h (solid line). After 18 h, the temperature (dotted line) is reduced to 30°C, whereupon another 3 wt.% of hydrogen is absorbed. This may be due to both chemisorption and physisorption phenomena occur in these materials and the mechanism is yet to be investigated. The reproducibility and reversibility with high hydrogen storage capacity of 3–10 wt.% at different temperatures in electrospun PANI nanofibers obtained in both the PCT and sorption kinetic measurements.

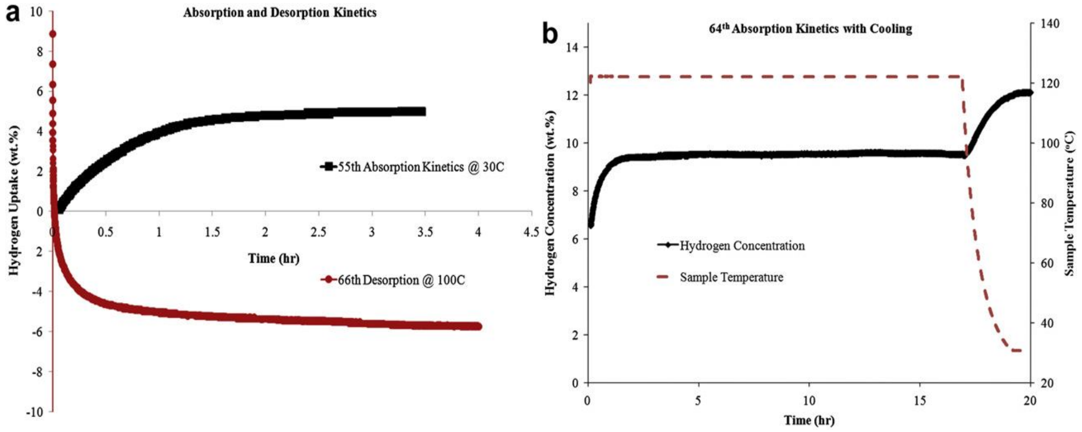


**Fig. 6**: Hydrogen sorption kinetic curves of PANI-NF electrospun samples at different cycles.

## 5. Conclusions

PANI nanofibers with help of PVA binder have been produced by simple Electrospin technique and also characterized for their structural and morphological properties. Polyaniline fibers were synthesized using chemical templating method followed by electrospinning process. The FTIR spectra of these PANI fibers reveal the presence of two bands in the vicinity of 1500 cm$^{-1}$ and 1600 cm$^{-1}$, which are assigned to the non-symmetric C6 ring stretching modes. The lower frequency vibration at 1500 cm$^{-1}$ is for the benzenoid rings, while the higher frequency mode at 1600 cm$^{-1}$ corresponds to benzenoid to quinoid transition indicating the synthesized polymer was polyaniline in oxidized form. The formed fibers have diameter close to 80 to 100 nm. A reversible hydrogen storage capacity of 3–10 wt.% was also found in electrospun PANI fibers at different temperatures (25–125°C). Further experiments are under progress to fine tune the storage capacity of nanofibers at particular operating temperature. Also it is planned to grow PANI nanofibers under different conditions using different solvents and binders to see their effect on hydrogen storage capacity.

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