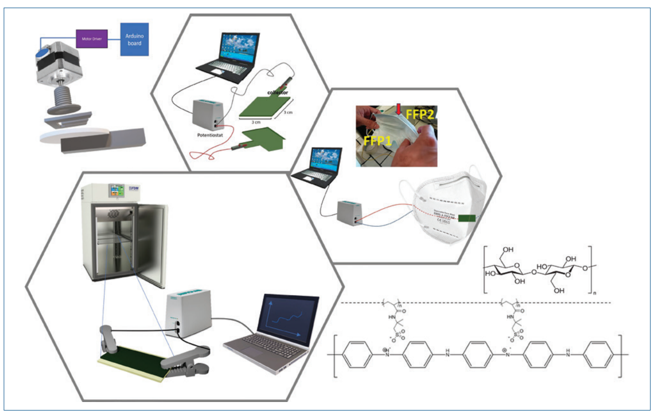
http://dx.medra.org/10.17374/CI.2024.106.1.44

Barbara Ballarin[a,b,c] Maria Cristina Cassani[a,b], Valentina Di Matteo[a], Lamyea Yeasmin[d], Isacco Gualandi[a,c]
[a]Department of Industrial Chemistry "Toso Montanari", Università di Bologna, and UdR INSTM, Bologna
[b]Center for Industrial Research-Advanced Applications in Mechanical Engineering and Materials Technology CIRI MAM, Università di Bologna
[c]Center for Industrial Research-Fonti Rinnovabili, Ambiente, Mare e Energia CIRI FRAME, Università di Bologna
[d]Politecnico di Torino
barbara.ballarin@unibo.it

A PROMISING MATERIAL FOR SENSORS AND BIOMEDICAL DEVICES

The excellent properties of a metal-free cellulose modified with polyaniline material (Cell/PANI) have been demonstrated by realizing proof of concept for touch sensors, humidity sensors, biomedical devices by successfully building electrocardiogram electrodes and sensors for monitoring the respiratory rate.



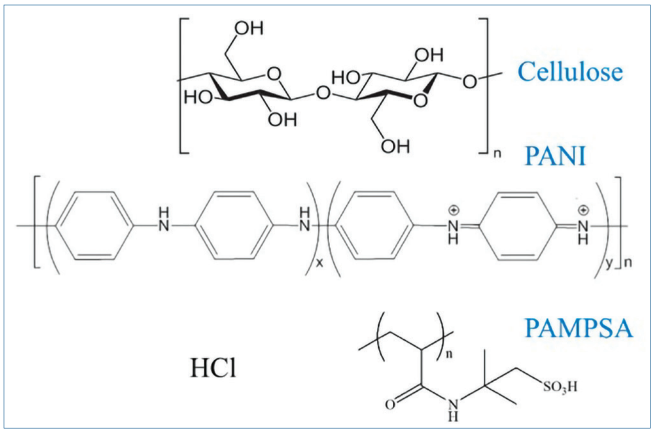
Introduction

Several daily life actions are eased by the presence of electrical devices but only 20% of these appliances is correctly recycled. Many landfills continue to be stuffed with unwanted electronics and workers are exposed to hazardous and carcinogenic substances during informally recycling processes in developing countries. As new products are consumed by hungry customers wanting the latest and greatest technology, the sheer volume of these daily produced discarded materials makes this task apparently insurmountable [1]. Research efforts are focused on the development of an alternative to traditional electronics that should be low-cost, degradable, compostable, and made from environmentally nontoxic substances.

Cellulose is one of the most investigated raw materials, mainly because of its high abundance on earth, biocompatibility, porosity, high flexibility and lightweight [2-4]. In addition, its low price (about 0.1 cent dm^{-2}) [5] and its recyclability make cellulose an economically viable option [6, 7]. Despite its high surface resistivity at relative humidity of 20-40% [5], it can be used as support to produce conductive paper that can be exploited in a wide range of applications, including supercapacitors, microfluidic systems, diagnostic devices, actuators and sensors [8, 9]. Two different approaches to prepare conductive paper are described in literature.

In the first one, organic or inorganic conductive, semiconductive and dielectric printable materials are deposited on paper employing screen, inkjet printing or flexographic techniques [5].

The second approach consists in embedding conductive materials such as functionalized multi-walled carbon nanotubes, inorganic nanoparticles and conducting polymers (CPs) in cellulose fibres making them conductive [2, 3, 10-12]. Conducting cellulosic fibres produced by coating with CPs (*i.e.* polyaniline (PANI), polypirrole (PPY), poly(3,4-ethylenedioxythiophene) (PEDOT) etc.) are being explored for various applications including supercapacitors, batteries, transistors, conductive wires, actuators and touch sensors [5, 13, 14].



Scheme 1

In this scenario PANI is particularly interesting because of its low cost, easy preparation, good environmental stability, and tuneable electrical properties by varying its oxidation state [15-18]. *In situ* polymerization is the most popular way of depositing PANI on cellulosic fibres. Different methods can be employed depending on the types of fibre, oxidants, medium, dopants, monomers, concentration used, processing steps and parameters [16, 19].

A simple, inexpensive, and easily scalable industrial paper process to prepare sheets of conductive cellulose fibres coated with polyaniline is herein presented. Firstly cellulose/PANI fibres were prepared in which PANI, in the form of protonated conductive emeraldine salt, was obtained by a simple *in situ* oxidative polymerization of aniline on bare cellulose fibres in acidic media [14, 20]. Two different acidic media have been used in order to assure the conductive oxidative state: chloridric acid HCl and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA) (Scheme 1). We have employed the following parameters: a fixed aniline to acid molar ratios of 1, a cellulose to aniline weight ratio of 1 and an excess of oxidizing agent. The final materials were washed several times with 1.0 M citric acid solution to completely remove the unreacted reagents. The biodegradability and biocompatibility of cellulose, chitin, chitosan, etc. in the matrix of PANI is widely reported in the literature [21, 22].

Successively, the fibres were assembled to give electroactive sheets with different thickness and resistivity. Finally, these electroactive sheets were tested as possible devices for different applications: i) capacitive and resistive touch sensors, ii) humidity sensors and iii) biomedical devices for EGC measurements and respiratory monitoring.

Preparation of electroactive sheets and devices

The modification of bare cellulosic fibres with PANI was obtained via a simple *in situ* oxidative polymerization of aniline in acid media, as recently described in our previous papers [2, 23, 24]. Two different acids have been used as PANI electrolytic dopant, HCl and PAMPSA (Cell/PANI and Cell/PANI_P, respectively). The introduction of PAMPSA was necessary for increasing the mechanical resistance of the device and makes it more biocompatible. The wet coupling method, employed in the paper industry, was used to prepare the Cell/PANI sheets of 0.4 mm thickness and a sheet resistance of 237±9 Ω sq^{-1} (specific conductivity of 0.1 S cm^{-1}) coupled with a bare cellulose sheet of 0.4 thickness for the applications as touch and humidity sensors [5]. Dimensions and shape of the final sensors can be easily varied as reported in Fig. 1.

As concern the sensors obtained with Cell/PANI_P, a similar fabrication process has been however used in this case a bare cellulose support was not necessary [24].

The Cell/PANI sheets were used for both t capacitive and resistive touch sensors. The capacitive component was measured without any touch interaction and during the dynamically induced increasing pressure up to a maximum value of 22 kPa (saturation level). The Cell/PANI sensor was excited by a square

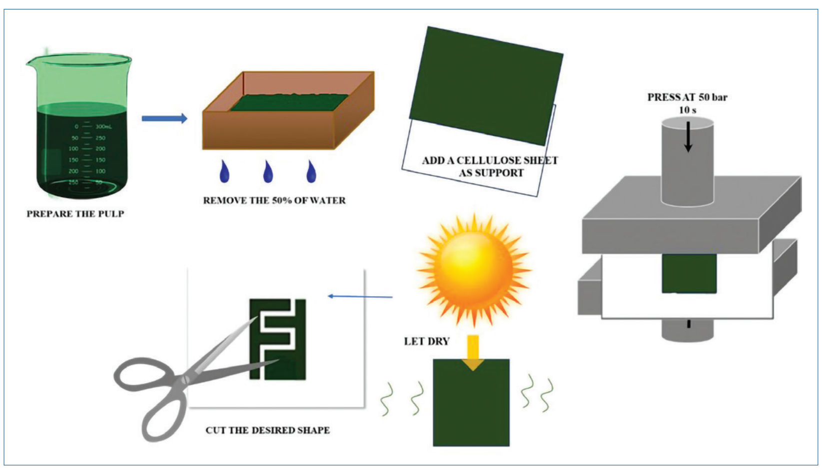


Fig. 1 - Scheme of sheets and devices fabrication process

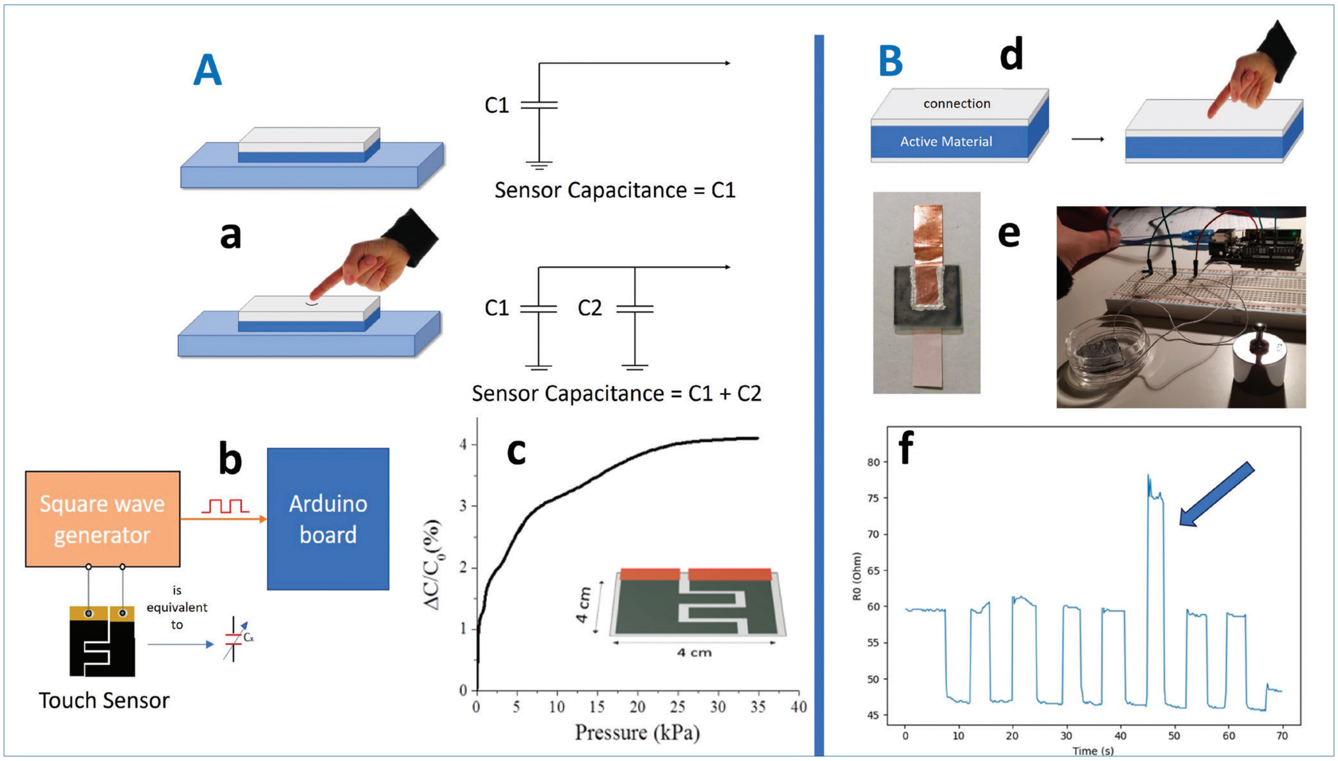


Fig. 2 - A) Capacitive touch sensors: a) scheme, b) Arduino stimulation, c) response curves; B) Resistive touch sensors: d) scheme, e) resistive sensor, f) response curve

wave through a Weight Force Generator (a mechanical force-weight actuator capable of exerting a gradual and constant pressure on the sensor surface) while the out-put signal was observed with the oscilloscope and acquired with Arduino Uno development board [2]. For what concerns the resistive sensors, a simple test was performed connecting the device with the dimension of 1.0 cm^2 with an Arduino Uno board and putting and removing a weight of 50 g on it.
As regards the humidity measurements, sensors areas of 2.2x0.9 cm size were obtained from Cell/PANI or Cell/PANI_P conductive sheets [23]. The tests in climatic chamber (ClimaCell 111 comfort, MMM Group) have been carried out at a fixed temperature of 21±1 °C following the chronoamperometric respond of the humidity sensor at an applied potential of 0.1 V. We set the steps uphill from 5% up to 55% RH, each step maintained for 1 hour and 15 min. (total time for each measure: 7.5 hours). A commercial digital-output relative humidity and temperature sensor/module DHT22 (also named as AM2302, Guangzhou Aosong Electronics Co.,Ltd, China) was used to monitor the % RH and temperature inside the climatic chamber at each measurement, for comparison.

For heart rate (EGC measurements) two square Cell/PANI-P electrodes with dimensions of 2.0 cm^2 were proceeded form the original sheet and connected with copper wire to the potentiostat. The electrodes were moistened before applications and were positioned directly on the body.
For the respiratory monitoring, a Cell/PANI_P rectangular sensor with dimensions of 5 cm^2 (1x5 cm) was proceeded form the original sheet and inserted between a FFP2 and FFP1 face mask, and then connected with the potentiostat. The current *vs* time curves were registered during a normal respiratory activity.

Results

Touch Sensors

Capacitive touch sensors are widely used in most of the portable devices such as mobile phones, but they are present even in home appliances, automotive and industrial applications. In this kind of devices, the electrode represents one of the plates of the capacitor. The second plate is represented by two elements: one is the environment of the sensor electrode which forms parasitic capacitor C1 and the other is a conductive object like a human finger which forms touch capacitor C2. A schematic representation of a capacitive touch sensor is shown

in Fig. 2A(a). The sensor is connected to a read-out electronics that measures the capacitance periodically. The output capacitance will increase if a conductive object touches or approaches the sensor electrode. The measurement circuit will detect the change in the capacitance and converts it into a trigger signal. The size and shape of the sensors but also the covering material will influence the sensitivity of the sensor.
Resistive touch sensors require an easier technology because they are not dependent by the properties of capacitance. Thus, conductive materials (*i.e.*, fingers) are not required to make the sensor works. Simply, a conductive material is interposed between two connections and the variation of resistance between touched and untouched material is detected Fig. 2B(d). The resistance decreases when the distance between the connections is reduced.
Fig. 2A (b and c) shows the results of the tests reporting $\Delta C/C_0\%$ *vs* pressure, where ΔC is (C_P-C_0), C_P and C_0 correspond to the capacity with and without pressure [2, 25]. The sensor curve reported in Fig. 2A(c) follows a logarithmic trend and shows sensitivities of 2.34 (0.45 σ%), 1.37 (0.44 σ%) and 0.19 (0.44 σ%) kPa-1 at pressures of 0.5, 2 and 20 kPa, respectively, each data is the average of five different measurements. Moreover, under each pressure, it displays a good and stable response. Finally, under a pressure around 6 kPa the sensors response time is of 52±1 ms.
As regards the resistive touch sensor, the set-up of the measurements is reported in Fig. 2B(e) and, as shown in Fig. 2B(f) the sensor exhibited a good response time (50±2 ms) and a repeatability under the same weight (50 g). Moreover, fast response is observable even with the increase of the weight (100 g).

Humidity sensors

Cell/PANI and Cell/PANI_P have been tested in a climatic chamber at a fixed temperature of 21 °C following the current response from 30 up to 50% RH. The RH range and temperature were chosen in accordance with the restrictions in which museums and buildings holding collections of cultural heritage objects are often maintained (50±5%RH and 20 or 21±2 °C) [23]. All the tests were compared with a commercial digital-output relative humidity and temperature sensor (DHT22) in parallel. The schematic representation of the used setup as well as the results are reported in Fig. 3.

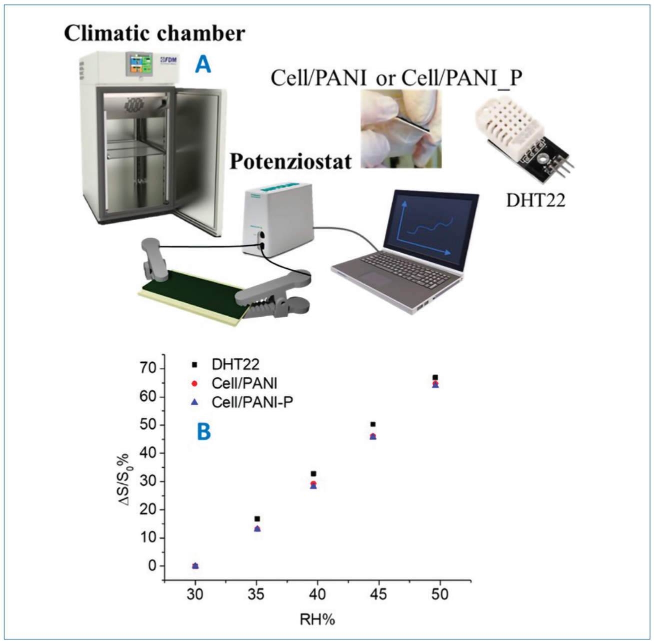


Fig. 3 - A) Climatic chamber setup and B) responses $\Delta S/S_0$ *vs* RH (calibration function: y = 3.34 x -102.10, y = 3.30 x -101.09 and y = 3.44 x -103.31 for Cell/PANI Cell/PANI_P and DHT22 respectively)

The responses $\Delta S/S_0$ (eq. 1) *vs* RH relationship of the Cell/PANI, Cell/PANI_P and DHT22 sensors

$$\Delta S/S_0\% = [(S-S_0)/S_0]100 \quad (1)$$

where S_0 is the signal of the sensor at 30% RH and S stands for the signal at targeted RH environment presents a good linearity (R^2=0.9979, R^2=0.9982 and 0.9998, respectively) in the RH% range investigated. The comparison of the slope of the curves: 3.34±0.11, 3.30±0.12 and 3.44±0.03 for Cell/PANI, Cell/PANI-PA and DHT22 respectively show that the rate of change response of the three sensors is clearly statistically equal [23].

Biomedical devices

Due to the fact that PAMPSA improves the mechanical properties of paper and helps to preserve the electrical properties after repeated mechanical deformation Cell/PANI_P were employed for biomedical devices preparation [24]. The non-cytotoxic and biodegradability of PANI_P polymers was previously reported in literature [21, 26].
Electrocardiogram (ECG) collecting bioelectrical signals with electrodes on the surface of the body, could give not only a clinical diagnosis of various heart diseases, but also represent a simple but effective tool to explain arrhythmia and conduction

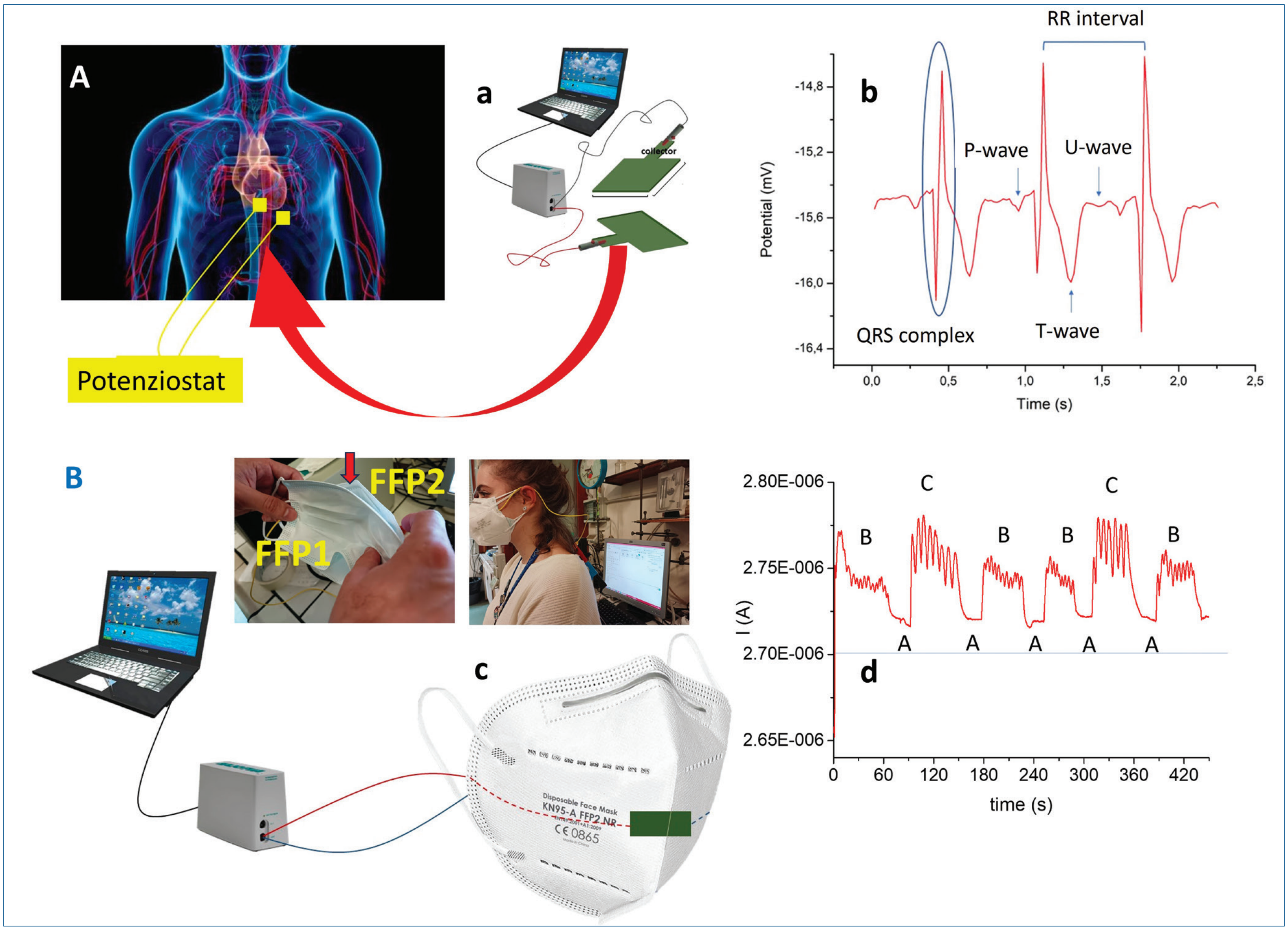


Fig. 4 - A: (a) EGC measurements set-up; (b) output ECG; B): (c) respiratory behaviour set-up;
(d) response curve for noise breathing rate (A = 30 s without breath; B = 60 s normal breath; C = 60 s fast breath)

disorders [27]. ECG sensors detect the polarization and depolarization of myocardial cells that generates electric current [28]. For the ECG measurements two square Cell/PANI_P electrodes were placed on the skin close to the hearth Fig. 4A(a) and the difference of voltage between the two electrodes was measured. Due to the conductive form of PANI_P, it is not necessary the use of a conductive gel and the two square electrodes can be directly positioned after moistened. The ECG output registered on a volunteer with a normal sinus rhythm is reported in Fig. 4A(b). The three main components of a typical ECG tracing can be recognized: P wave, which represents depolarization of the atria, QRS complex, which represents depolarization of the ventricles and the T wave which represent repolarization of the ventricles. In healthcare, variations in respiratory frequency can be used as predictors of physiological deterioration and serious adverse events. In sport and physical activity, respiratory frequency is a valid marker of physical effort and is associated with exercise tolerance in different populations [29, 30]. The response curve for noise breathing rate obtained interspersing 30 s without breathing (A) with normal (B) or fast (C) breathing is reported in Fig. 4B(d). The data are reported without processing the signal, normally necessary to eliminate the baseline drift of respiratory rate response curve. In the absence of breathing, the signal is flat, in accordance with a stable humidity value inside the mask. Instead, during respiration, the current value fluctuates due to the humidity variation generated by respiration. The greater the intensity of breathing, the greater is signal oscillation. The data show that the sensor can measure the respiratory rate by also identifying the intensity of respiration.

Conclusion

Conductive paper sheets based on cellulose and PANI with excellent electrical performances can be produced via an easily scalable industrial paper process.

This method can provide an enormous improvement in the field of low-cost electronic technology. The capacitive touch sensors show a very quick response time (52 ms), and a sensibility that can be easily modulated by changing the geometry of the device. The humidity sensors showed a linear and rapid response and a stability in the signal for short and long-time humidity cycling. Moreover, the rate of change response of devices results perfectly comparable with that of a commercial digital output of a relative humidity and temperature sensor highlighting the promising performance in low-cost humidity monitoring.
The introduction of PAMPSA, used as a polyelectrolytic dopant in replacement of HCl increases the mechanical resistance of the Cell/PANI and reduces the loss of the acid counter-ion at higher pH contributing to the stability of the oxidative state of PANI form up to pH 10 and increasing its biocompatibility. The excellent properties of Cell/PANI-P have been demonstrated by realizing proof of concept biomedical devices based on this material by successfully building electrocardiogram electrodes, without using any electrode gel, respiratory sensors. The integration of the humidity sensor inside a mask allows to monitor the respiratory rate of the wearer with the possibility of distinguishing the intensity of the breath. The estimate cost of Cell/PANI or Cell/PANI_P sensors results ca. 0.33 USD, cheaper than those on the market, normally between 4 and 9 USD. The results presented in this work clearly show the excellent properties of Cell/PANI as a material for paper electronics, paving the way for new fascinating applications.

References

[1] Report EU 2020. Web Site n.d. **https://www.unenvironment.org/news-and-stories/press-release/un-report-time-seize-opportunity-tackle-challenge-e-waste.**
[2] I. Ragazzini, I. Gualandi *et al., Carbohydr. Polym.*, 2021, **254**, 117304.
[3] D. Tobjörk, R. Österbacka, *Adv. Mater.*, 2011, **23**, 1935.
[4] A. Khan, Z. Abas *et al., Sensors*, 2016, **16**, 1.
[5] Y. Luo, J. Huang, *Sci. China Chem.*, 2014, **57**, 1672.
[6] A. John, S.K. Mahadeva, J. Kim, *Smart Mater. Struct.*, 2010, **19**, 045011.
[7] S. Kanaparthi, S. Badhulika, *Sensors Actuators: B Chem.*, 2017, **242**, 857.
[8] N.D. Sanandiya, Y. Vijay *et al., Sci. Rep.*, 2018, **8**, 1.
[9] Q. Wang, J. Sun *et al., Cellulose*, 2018, **25**, 4275.
[10] P. Das, V.C. Mai, H. Duan, *ACS Appl. Polym. Mater.*, 2019, **1**, 1505.
[11] L.E. Silva, P.I. Cunha Claro *et al., Cellul. Chem. Technol.*, 2019, **53**, 775.
[12] K. Sharma, K. Pareek *et al., Int. J. Energy Res.*, 2019, **43**, 604.
[13] R. Aguado, D. Murtinho, A.J.M. Valente, *Nord. Pulp. Pap. Res. J.*, 2019, **34**, 395.
[14] Z. Ma, W. Wang, D. Yu, *J. Mater. Sci.*, 2020, **55**, 796.
[15] N. Shoaie, M. Daneshpour *et al., Microchim. Acta*, 2019, **186**, 465.
[16] A.T. Singh, D. Lantigua *et al., Sensors*, 2018, **18**, 1.
[17] P. Singh, S.K. Shukla, *J. Mater. Sci.*, 2020, **55**, 1331.
[18] Y. Wang, A. Liu *et al., Polym. Int.*, 2019, **69**, 7.
[19] S. Ke, T. Ouyang *et al., Macromol. Mater. Eng.*, 2019, **304**, 1.
[20] Q. Shao, Z. Niu *et al., Small*, 2014, **10**, 1466.
[21] M. Shahadat, M.Z. Khan *et al., Adv. Colloid. Interface Sci.*, 2017, **249**, 2.
[22] Y. Arteshi, A. Aghanejad *et al., Eur. Polym. J.*, 2018, **108**, 150.
[23] I. Ragazzini, R. Castagnoli *et al., RSC Adv.*, 2022, **12**, 28217.
[24] I. Ragazzini, I. Gualandi *et al., Carbohydr. Polym.*, 2023, **316**, 121079.
[25] P. Cataldi, S. Dussoni *et al., Adv. Sci.*, 2018, **5**, 1700587.
[26] P. Bober, P. Humpolíček *et al., RSC Adv.*, 2015, **5**, 50328.
[27] M.K. Yapici, T.E. Alkhidir, *Sensors*, 2017, **17**, 1.
[28] M.S. Al-Ani, *UHD J. Sci. Technol.*, 2018, **2**, 7.
[29] A. Al-Halhouli, L. Al-Ghussain *et al., Sensors*, 2021, **21**, 1.
[30] S. Kano, N. Jarulertwathana *et al., Sensors*, 2022, **22**, 1.

Un materiale promettente per sensori e dispositivi medici

Sono state dimostrate le eccellenti proprietà di un materiale a base di cellulosa modificata con polianilina (Cell/PANI) tramite la realizzazione di sensori tattili, sensori di umidità, dispositivi biomedici, costruendo con successo elettrodi per la misura di elettrocardiogrammi e sensori per il monitoraggio della frequenza respiratoria.