Flexible camphor sulfonic acid-doped PAni/ α -Fe₂O₃ nanocomposite films and their room temperature ammonia sensing activity

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Abstract

Composite nanostructures play a crucial role in gas sensing applications owing to their tunable properties and sizes. The main goal of this article is to prepare camphor sulfonic acid (10-50 wt %)-doped PAni/ α -Fe₂O₃ (PFC) composite nanostructured films on flexible polyethylene terephthalate (PET) substrate through in-situ polymerization process and study their gas sensing activity towards various gases. Structural and morphological measurements along with gas sensing properties in terms of selectivity, response, stability, and response-recovery times are investigated and reported. The gas selectivity tests of flexible PFC nanostructured composite films are performed towards different gases such as NO₂, NH₃, LPG, CH₃OH, and C₂H₅OH etc., wherein all the flexible PFC (10-50%) films demonstrate a superior selectivity towards NH₃ gas even in the presence of other test gases. Among the different compositions, 30% PFC flexible film exhibits highest response of 72% to 100 ppm NH₃ with good response time of 65s. The systematic study between PFC flexible nanocomposite films and NH₃ gas is conducted and

reported. In addition, the interfacial charge transfer kinetics across NH_3 and PFC film interface was investigated by means of impedance spectroscopy study.

Keywords: Hybrid nanocomposite; Flexible films; Gas sensor; Impedance spectroscopy;

1. Introduction

Flexible gas sensors have a broad range of application areas e.g. fertilizer and chemical industries. With increasing market demand, host of attempts for the improvement of gas sensing performance in terms of selectivity, sensitivity, stability, and operation at room temperature have been made to rationalize miniaturized design of a sensor [1-3]. The most crucial criteria for the fabrication of a good sensor is that it should operate at room temperature and have the ability to detect gas below a threshold considered to be acceptable by relevant institutions such as Environmental Protection Agency (EPA). According to EPA criteria, NH_3 is hazardous above 25 ppm. 90% of all NH_3 emissions are generated from livestock waste management and fertilizer production. As a result sensing hazardous NH_3 at low ppm requires low cost and highly sensitive room temperature operating gas sensor systems. In view of sensing materials feature, among the conducting polymers (such as polythiophene, polypyrrole, and polyaniline (PAni)), PAni is used as a potential material for NH_3 gas sensing applications due to its attractive redox properties [1-5]. Among the conducting polymers, PAni is the most suitable polymer for being either doped or de-doped by the addition/removal of H^+ ions at backbone [4-6]. However, polymer based gas sensors have a poor stability due to exposure of temperature and moisture in the environment, which impairing the long term sensing performance [7, 8]. In contrast, gas sensors prepared using metal oxides such as tungsten oxide (WO_3), tin oxide (SnO_2), iron oxide (Fe_2O_3), and zinc oxide (ZnO), exhibit better stability and superior sensing characteristics, caused by oxygen

stoichiometry change, but their higher operating temperature (200-400 °C) limits practical and commercial use [9-11]. Room temperature gas detection is a notable property of conducting polymer sensors [4-6]; therefore, it is necessary to modify the properties of conducting polymers in order to remove their existing drawbacks. The functional properties of conducting polymer-based gas sensors can be improved by incorporating metal oxide nanoparticles into the polymer matrix [11-16]. The properties of the prepared organic-inorganic nanocomposite materials differ from their original component, depending on their morphologies and interfacial characteristics [12-16]. Organic-inorganic composite materials have attracted significant attention in gas sensing applications due to their room temperature operation capability, long life and selectivity [12, 13, 17]. Combination of two different phases of organic and inorganic materials is a great challenge in designing the nanocomposite sensors. Flexible sensors prepared in aqueous media using organic-inorganic materials such as PANi and α -Fe₂O₃ during the de-doping of PANi by ammonia solution is limited by poor solubility [15], leading to less active sites available for adsorption of gas molecules, which indirectly limits the performance of sensor.

In the present study, for further boosting the sensing properties, improving stability against temperature, and repeated gas exposure cycles, PANi/ α -Fe₂O₃ (PF) nanocomposite was doped with camphor sulfonic acid (CSA) by *in-situ* polymerization [18, 19]. The dopant CSA increased the dispersion of α -Fe₂O₃ into the PANi matrix, and thus generated more active sites to analyte species [20]. Previously CSA has been considered to be a potential dopant for increasing conductivity and stability of PANi composites [21, 22]. In present study, CSA is acting as a surfactant due to which; a) maximum number of PANi/ α -Fe₂O₃ nanoparticles on PET substrate can be anchored, and b) changes the morphology of PANi from compact granular dense structure to well-developed fibrous structure [20-25].

For the first time, we report the synthesis of CSA-doped PF nanocomposite flexible films (*in-situ* synthesis of formation of flexible PFC nanocomposite films is shown in Scheme 1) and compare them with the results available in literature [20-22]. From the obtained results, it is concluded that, the flexible PFC films have potential to detect NH_3 below hazardous concentrations at room temperature. Therefore, the present sensor films and method of preparation are useful for gas sensing applications, such as monitoring the air quality in industrial facilities and other applications, where detection of NH_3 is crucial.

Scheme 1: Synthesis of PFC nanocomposite flexible films.

2. Experimental details

2.1 Chemicals

Aniline ($\text{C}_6\text{H}_5\text{NH}_2$) (99%), ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$), methanol (CH_3OH), and hydrochloric acid (HCl) (35% conc.); all AR grade chemicals were purchased from sd-fiNE

chemicals PVT Ltd. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was used as a source for iron oxide and dopant CSA ($\text{C}_{10}\text{H}_{16}\text{O}_4\text{S}$) was purchased from Aldrich.

2.2 Synthesis of $\alpha\text{-Fe}_2\text{O}_3$

A sol-gel method was employed for the synthesis of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles. In a typical experiment, 1.693 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added in 50 mL of CH_3OH and the desired mixture stirred vigorously at 60 °C until the formation of brownish colored powder, which was collected and washed several times with CH_3OH and dried. Finally, the dried powder was annealed in furnace at 700 °C for 1 hr to obtain nanocrystalline $\alpha\text{-Fe}_2\text{O}_3$.

2.3 Formation of PFC films

Highly uniform and flexible PFC nanocomposite films were prepared by a simple and facile in-situ polymerization method [15]. Initially, $\text{C}_6\text{H}_5\text{NH}_2$ monomer was polymerized by using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as an oxidant in presence of 1M HCl solution. Sol-gel processed $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles were used for the nanocomposite formation. PANi/ $\alpha\text{-Fe}_2\text{O}_3$ composite was prepared by adding 0.5 gm of $\alpha\text{-Fe}_2\text{O}_3$ in polyaniline solution during de-doping by NH_3 . CSA was separately added with varying weight percent (10-50 wt%) in PF composite solution and whole solution was kept for 5 hr stirring. Flexible PET substrate was dipped into the PFC solution during stirring. After the polymerization process, a thin layered PFC composite flexible film was formed, which was further characterized for its structure, morphology, phase purity, and gas sensing measurements.

2.4 Characterization tools and gas sensing measurements

X-ray diffraction pattern (XRD) of prepared films were obtained with Rikagu Altima-IV diffractometer using Cu-K_β radiation source ($\lambda=1.5406\text{\AA}$) with continuous scan at 40kV and 40mA. Fourier transform infrared (FTIR) and RAMAN analyses were carried out on Perkin-

Elmer 100 spectrophotometer and Hololab series-5000 Raman spectroscopy, Kaiser Optical Systems, Inc., respectively. Morphology of prepared films was observed by Field emission-scanning electron microscopy (Model: FE-SEM MIRA3 TESCAN). Impedance measurements were conducted using Wayne Kerr 6500B impedance analyzer in the frequency range of 20 Hz to 10 MHz.

Gas sensing measurements on prepared samples were carried out using a procedure described elsewhere [15]. In order to measure the sensing characteristics of PFC nanocomposite films, the sensor films were mounted into two probe air tight gas chamber, which was connected to the computer interfaced 6514 programmable electrometer. The change of resistance on exposure to the analyte was measured at a time interval of 1 s. The response of flexible films towards different gas exposure cycles was calculated by measuring the resistance of sensor in air (R_a) and resistance of sensor in gas (R_g) using following formula:

$$\text{Response, } S (\%) = [(R_g - R_a) / R_a] \times 100 \quad (1)$$

3. Results and discussion

3.1 Structural analysis

The XRD pattern of PAni, α -Fe₂O₃, and 10-50 wt% PFC nanocomposites is shown in fig.1 (A). The observed broad peak, between 20–30° (2 θ), in the XRD pattern of PAni (fig.1 (a)) confirming the amorphous behavior of synthesized PAni [12, 13, 15]. The observed peak positions in fig.1 (b) at 24.08°, 33.01°, 35.59°, 40.87°, 49.52°, 54°, 57.64°, 62.36°, 64.01°, and 71.94° (2 θ values) are in concurrence with the reported values for α -Fe₂O₃ (JCPDS Card no. 89-596) [12, 15]. The XRD patterns of 10-50 wt% PFC nanocomposite flexible films are shown in fig. 1(c-g), wherein the presence of sharp peaks, suggesting high crystallinity of the products, was confirmed. The obtained peak positions are well-associated to α -Fe₂O₃, demonstrating that

structure of $\alpha\text{-Fe}_2\text{O}_3$ cannot be tailored in the presence of PANi and CSA. The wide peak in between $20^\circ\text{-}30^\circ$ represents the mixture of both the phases of crystalline $\alpha\text{-Fe}_2\text{O}_3$ and amorphous PANi. The broad peak of PANi flattened upon increasing the CSA concentration. Also, the full width half maxima of $\alpha\text{-Fe}_2\text{O}_3$ peaks found to decrease with respect to CSA concentration, signifying an addition of CSA in PF composite induces some crystallinity. Average crystallite size was calculated, along highly preferred (104) plane, using renowned Debye-Scherrer relation and it was found to be ≈ 43 nm for $\alpha\text{-Fe}_2\text{O}_3$, ≈ 44 nm for 10% PFC, ≈ 45 nm for 20% PFC, ≈ 47 nm for 30% PFC, ≈ 50 nm for 40% PFC, and ≈ 52 nm for 50% PFC. FTIR study was carried out to get insights into the chemical structure of prepared PANi, $\alpha\text{-Fe}_2\text{O}_3$, and PF nanocomposite with the varying concentration of CSA (10-50 wt%) [Fig. 2 (B)]. The FTIR spectrum of PANi (Fig. 2 (a)) shows the characteristic peaks at 565, 804, 1061, 1198, 1283, 1496, 1597, and 1719 cm^{-1} ; which are belongs to C-H out of plane bending vibration, C-H out of plane bending vibration in para-disubstituted benzene ring, C-H in plane bending vibration, C-H in plane bending, C-N stretching vibration, C-C stretching of benzenoid ring, C=C stretching of quinoid ring, and C=O stretching vibrations, respectively [12-15, 20, 22]. The FTIR spectrum of $\alpha\text{-Fe}_2\text{O}_3$ (Fig. 2 (b)) showed the characteristic peak at 594 and 642 cm^{-1} which are due to the metal-oxygen (Fe-O) vibration [12, 15, 26]. The peaks located at 712 and 916 cm^{-1} are due to the Fe-OH vibration modes [19, 21]. Whereas, the peaks situated at 1605 cm^{-1} is attributed to the hydroxyl group [21, 25, 26]. The FTIR spectrum of 10-50 wt. % PFC nanocomposites is shown in fig. 2 (c-g)), wherein the characteristic peak observed at 566 cm^{-1} corresponds to the Fe-O bonding of iron oxide and that of 805 cm^{-1} is of C-H out of plane bending related to PANi [26, 27]. The peak at 1040 cm^{-1} is the characteristic of sulphonated PF nanocomposite [28]. The other peaks observed at 1135 cm^{-1} and 1297 cm^{-1} are due to the B-NH=Q vibration and C-N stretching modes

correspondingly [26, 29]. While, the absorption peaks located at 1490 cm^{-1} and 1570 cm^{-1} are attributed to the C=C stretching mode of benzoid and quinoid ring of PANi, respectively [26, 28, 29]. The absorption peak observed at 2832 cm^{-1} is associated with N-H vibration in benzenoid ring [30]. Thus, from the FTIR analysis shift in PANi and $\alpha\text{-Fe}_2\text{O}_3$ peak positions, due to the addition of CSA, were observed, which demonstrates the strong interaction between PANi, $\alpha\text{-Fe}_2\text{O}_3$, and CSA.

3.2 Optical analysis

UV-visible spectrums of 10-50% flexible PFC nanocomposites are highlighted in fig. 1(C). The characteristic absorption band observed at 709 nm indicates the presence of the emeraldine form of PFC nanocomposites due to the de-doping by the ammonia solution, while the absorption bands at 451 nm and 812 nm are assigned to polaron to π^* and π to polaron transitions, respectively. This clearly corroborates that the composites made in aqueous medium are conductive due to CSA doping [23-25].

3.3 Raman spectroscopy

Raman spectroscopy is an efficient method to study the different chemical bonds present in the material. Raman spectra of PF and 30% PFC nanocomposite are shown in fig. 2(a) and (b), respectively. The addition of CSA in PF nanocomposite shows the shifting of Raman bands towards higher wave number side when compared to PF. The characteristic Raman band observed at 1347 cm^{-1} and 1563 cm^{-1} are caused by the C-N⁺ stretching vibration and C-C stretching of benzenoid ring, respectively. While the lower intensity band located at 639 cm^{-1} belongs to oxidized state of aniline oligomers, which are associated to the $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles [31, 32].

3.4 Compositional analysis

Distribution of CSA and α -Fe₂O₃ nanoparticles in PANi matrix was confirmed by using the energy dispersive X-ray analysis (EDAX). EDAX spectrum of 30% PFC nanocomposite is shown in fig. 2(c), which shows more intense peak of C and N due to PANi. Peaks of Fe, S, and O are also observed with lower intensity. EDAX spectra confirm the presence of α -Fe₂O₃ and sulfonic group in polymer matrix.

3.5 Surface morphology

It is well-known that the surface structure and morphology of the materials are crucial in gas sensing applications [33, 34]. Morphologies of prepared flexible films were analyzed by FESEM [fig. 3]. The FESEM micrographs of PF nanocomposite film (Fig. 3(a)), prove the α -Fe₂O₃ nanoparticles being uniformly dispersed on the surface of the dense PANi fibers network. The addition of 10-50 wt% CSA strongly affects on the surface morphology of PF nanocomposite fig. 3(b-f), showing that α -Fe₂O₃ nanoparticles are completely covered by the PANi fibers. Also, 10-50 wt% PFC surface is porous, well-developed and of interconnected type. It is to be noted that such type of porous fibrous structure provides a high surface-to-volume ratio and help to diffusing gas easily resulting in a reaction rate enhancement [35-37]. The porous structure of PFC film can help facial absorption and desorption of NH₃ gas molecules, because a faster and stronger interaction between sensor surface and NH₃ gas can be anticipated.

3.6 Gas sensing properties

Gas sensing measurements of as-prepared PFC films were carried out towards various gases such as LPG, CH₃OH, NO₂, NH₃, and C₂H₅OH, at room temperature. It is well-known that the gas sensors operate on a principle of resistance change due to the adsorption of gas molecules [38]. Sensors transform the analyte's chemical energy into detectable electrical signals such as a

change in resistance, voltage, or current. In present case, we recorded the change in sheet-resistance as a function of time upon exposure to different gases.

3.6.1 Selectivity

For the selectivity study and to understand the influence of CSA on the gas sensing properties of PF nanocomposite films, the sensing performance was examined at 100 ppm concentration of different oxidizing and reducing gases. Before the gas sensing measurement, an individual flexible sensor film was mounted in the gas sensing chamber for baseline resistance stabilization at room temperature. The selectivity bar chart of 30 wt% flexible PFC film is shown in fig. 4 (a), revealing that PFC films possess superior selectivity towards NH_3 in comparison to other gases i.e. the response of NH_3 is ~17 times larger than NO_2 , the second ranking gas. Therefore, the further study, NH_3 is used as a target gas for PFC films. The plot of response as a function of CSA concentration to 100 ppm NH_3 of flexible PFC film is shown in fig. 4 (b). Out of different CSA concentrations, 30 wt% PFC film showed the higher response of 72%. Therefore, instead of showing the selectivity to each CSA concentration, we have selected the selectivity study of simply 30 wt% PFC flexible film (fig. 4(a)). The response values of 10-50 wt% PFC films are 48%, 62%, 72%, 68%, and 56%, respectively, to 100 ppm NH_3 operating at room temperature. Plot of response vs. time for 10-50 wt. % PFC film is shown in the inset of fig. 4 (b). Increase in resistance value after the interaction of NH_3 with PFC film is noticed. When the outlet was opened and fresh air introduced into the chamber, resistance of sensor decreased and reached to its original baseline value. Initially sensor resistance is increased and reached to its maximum value and then again decreased because of the desorption process.

3.6.2 Response study

The sensing performance of PFC flexible films was evaluated in terms of percentage response and response/recovery characteristics by exposing it to different NH_3 (2.5-100 ppm) concentrations. Fig. 5(a) shows the comparative plot of changes in sensing response against time to different NH_3 concentrations (2.5 ppm-100 ppm) at room temperature. At 2.5 ppm of NH_3 , the gas sensor exhibits good response of 4% with response time of 434 s. While at higher gas concentration (100 ppm) it shows a maximum response of 72% with short response time of 50 s. It can be seen that flexible PFC films exhibit nearly linear response (see inset of fig.5 (a)) to NH_3 gas from 2.5 ppm to 100 ppm. The change in response is mainly related to the concentration of NH_3 gas. A higher response at higher concentration indicates that there is maximum number of active interaction sites available on PFC nanocomposite surface for the adsorption of NH_3 gas [39].

3.6.3 Reproducibility study

Repetitive responses of flexible PFC films to 100 ppm exposure of NH_3 gas were also carried out [fig. 5(b)]. The reproducibility study showed that the PFC film is demonstrating a stable response and is also achieving a good reproducibility of the baseline resistance value for different NH_3 cycles, which is caused by the fact that the resistance of sensor returned to its original baseline due to the ability of PANi to restore its initial energy level and achieve baseline resistance stability after exposure to air. Physically adsorbed NH_3 molecules react strongly with PFC nanocomposite sensor film and can easily desorbed due to redox reaction taking place on the sensor surface. The reproducibility study revealed that the sensor based on flexible PFC film can be used as potential material for the detection of toxic NH_3 .

3.6.4 Response-recovery and stability study

The response-recovery characteristic is another major analysis used to estimate the performance of a gas sensor. The response-recovery characteristic of PFC flexible sensor was measured by number of gas exposure cycles with varying NH_3 (from 2.5 ppm to 100 ppm) concentration and presented in fig.5(c). Response-recovery characteristic demonstrates that with lower concentration (2.5 ppm) of NH_3 gas, the sensor required longer time duration (434 s) to reach its peak value, while recovery time is relatively fast (144 s). Conversely, at higher NH_3 concentration (100 ppm), the sensor reached its peak value within a short interval (50 s) while returning slowly to its baseline value (1575 s). The experimental results of PFC nanocomposite sensor are summarized in Table 1. It is observed that the sensor parameters change with the NH_3 concentration. Response of sensor is increased with the concentration of gas but contrasting results are observed in the case of response and recovery times. As the NH_3 concentration is increased then the response time dropped from 434 s to 50 s conversely recovery time is increased from 144 s to 1575 s. At lower NH_3 concentration, the number of H^+ ions removed from N site of PANi backbone is relatively small therefore they can restore original energy level very easily. Whereas, at higher concentration of NH_3 gas, the number of H^+ ions removed from N site of PANi backbone are more numerous therefore they require more time to restore original energy level. Therefore, response time is found to increases and recovery time is decreases with increasing NH_3 concentration. The stability study of flexible PFC sensor film is shown in the inset of fig. 5(c). Flexible PFC film exhibited excellent stability of 97% in a period of 25 days of measurements which furthermore tends to stabilize after 10 days. The response loss with time is attributed to the poor strength of PANi chains over a long period. Also, cyclic de-doping of PANi by NH_3 gas has adverse effect on the reaction rate [40].

3.6.5 Gas sensing mechanism

The probable gas sensing mechanism of the PFC nanocomposite flexible sensor can be described on the basis of variation in resistance (due to the redox reaction) after the interaction of NH_3 . The relative response of sensor depends upon the how much surface is available to adsorb the gas molecules. Therefore, the response and selectivity of gas sensors primarily depend on the density of active sites on the sensor surface that will adsorb target molecules. The redox reactions are expecting between the sensor surface and the target molecules (herein NH_3). PANi is a *p*-type material with the majority of charge carriers as holes and NH_3 is a reducing (electron donating) gas. When NH_3 interacts with PFC sensor at that time it withdraws protons from the –NH– site of conjugated PANi, due to this there is decrease of the hole density on PANi backbone resulting increase of sensor resistance. Because of accepting the H^+ ions from PANi backbone, we believe that there is a conversion of NH_3 to NH_4^+ ions (fig.6). The replacement of NH_3 gas by air reverses the process and thereby, the resistance decreases to its original value. This removal and addition of H^+ ion on –NH– site of PANi can form a pair of reversible reaction on the sensor surface [15, 41].

3. 7 Impedance spectroscopy

An impedance spectroscopy study was performed to gain the more information about interaction of NH_3 gas with PFC nanocomposite flexible sensor film. The observed experimental and fitted data of PFC nanocomposite flexible films in presence of air and NH_3 gas are given in fig. 7. The results exhibit a semicircle from the higher frequency region to the lower frequency region and the plot of real impedance (Z') vs. imaginary impedance (Z'') shows the good agreement between the experimental and fitted data.

The experimental data was fitted by using the following equation:

$$C=1/2\pi fZ' \quad (2)$$

The RC equivalent circuit (shown in inset of fig. 7) was used while fitting the experimental data. Here 'R₀' is the frequency independent resistance measured from the highest frequency region when 'R₁' and 'C₁' are in parallel. The calculated values of these parameters are shown in Table 2. Impedance results also confirm that the resistance value of flexible PFC film is increased after the interaction of NH₃ which is in good agreement with the results obtained from gas sensing study, discussed above.

4. Conclusions

Flexible PFC nanocomposite thin films were successfully prepared by a simple and unsophisticated *in-situ* polymerization method and applied for the application of detection of toxic gases. Structural, morphological, and compositional analyses revealed that the formation of PFC nanocomposite and also the insight interaction between CSA, PANi, and α-Fe₂O₃. Gas sensing measurements demonstrate that among different CSA concentration, 30 wt% PFC flexible films are highly sensitive to NH₃ gas and have exhibited maximum response of 72% (at 100 ppm NH₃) at room temperature with fast response time of 50 s. In addition, flexible PFC films capable to detect as low as 2.5 ppm concentration of NH₃. Thus, an in-situ polymerized flexible PFC film paves the approach for the development of low-cost NH₃ sensors. Hopefully, the observed results create a new path for further preparation of other nanocomposites with CSA.

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Figure captions:

Fig.1: (a) XRD, (b) FTIR, and (c) UV-Vis spectrums of 10-50% flexible PFC nanocomposite films.

Fig. 2: Raman spectra of (a) PANi/ α -Fe₂O₃ and (b) 30% PFC film, (c) EDAX spectrum of 30% PFC film.

Fig.3: FESEM images of; (a) PANi/ α -Fe₂O₃, (b) 10% CSA, (c) 20% CSA, (d) 30% CSA, (e) 40% CSA, and (f) 50% CSA doped flexible PF nanocomposite films, respectively.

Fig.4: (a) Selectivity study of 30 wt% PFC film, and (b) response of composite sensor for different CSA concentration (inset response vs. time graph of PFC films).

Fig.5: (a) Response to different NH₃ concentration, (b) reproducibility study, and (c) Response-recovery characteristics of flexible PFC sensor (inset shows stability study of PFC sensor).

Fig. 6: Gas sensing mechanism of PFC nanocomposite with NH₃.

Fig.7: Impedance spectra of flexible PFC film in presence of air and gas (inset shows the equivalent circuit used for fitting the spectra).

Table captions:

Table 1: Gas sensing performance parameters of flexible PFC sensor films.

Table 2: Parameters of equivalent circuit used for fitting the impedance spectra.