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The effect of film thickness and counter ions on the double layer and redox capacitance of polyaniline thin film electrode

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Abstract

The high and low frequency capacitances of polyaniline electrode in different acid medium were analyzed as a function of counter ions, redox states and film thickness. The corresponding double layer and redox capacitances were discussed in terms of variables affected in the growth of polyaniline film. The redox capacitance has been found to be predominant over double layer capacitance in the overall capacitance of the polymer film in the given electrolyte composition and a comparative analysis have been made. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polyaniline electrode; Double layer capacitance; Redox capacitance; Film thickness

1. Introduction

Polyaniline is the major attractive candidate in the family of conducting polymer by virtue of its demonstrated use in electrochromic devices [1,2], supercapacitative materials [3], intercalating electrodes in advanced batteries [4], electrocatalysis [5–7], microelectronic devices [8], etc. Among these applications, its use as supercapacitative element gains increasing attention [3–6], as the PANI electrodes are high surface area electrodes by virtue of high porosity of the film synthesisable by various methods [7].

Further, the porosity and surface area of polymer/electrolyte greatly depends on the redox state of polymer as this feature can be exploited to produce high energy density electrodes for supercapacitor. This feature is further complimented by low cost, high charge density, cycle life and thermal stability for its efficient use. The overall capacitance exhibited by PANI film is known to arise from the contribution of double layer capacitance and redox capacitance [9]. The distinction between these two capacitance has been recently highlighted by Grzeszczuk and Poks [10], by impedance spectroscopy analysis in aqueous trichloroacetic acid for polyaniline films. This gives rise to the possibility of quantifying the two different capacitance observable in conducting polymer electrode/electrolyte interface under various synthetic variables. Hence our objective in this work is focused to examine the PANI film impedance response over a wide range of potential for films formed to various thicknesses while employing several different acids in electrochemical growth conditions on Pt electrode. The principal goal is confined to evolve a better understanding of double layer and redox capacitance in the overall capacitance of the film from a careful variation of experimental parameters within a single controlled study.

2. Experimental

Polyaniline films were grown potentiodynamically on Pt (BAS electrode) from a solution of aniline and the acid using a reported procedure [11]. The acids used were HCl, H_2SO_4, HBF_4, and $HClO_4$. Typically PANI was deposited on a Pt electrode from a 1 M aniline-2 M acid using potential cycling at $0.05\,V\,s^{-1}$ between 0 and 0.7 V (vs. SCE) with first two scans being switched at 0.8 V instead of 0.7 V. Thickness of the polymer films were estimated based on the charge used in the reversible redox switching polyaniline [12]. Electrochemical impedance spectroscopy (EIS) measurements were carried out in 2 M aqueous solutions of different acid using EG&G (PARR) Electrochemical Impedance Analyzer. The d.c. potential range of measurements corresponds to the reversible process of polyaniline (i.e.) ranged from 0.2 to −0.7 V. The a.c. signals used were 5 mV in amplitude. The frequencies ranged from 100 kHz to 0.1 Hz. The Boukamp [13] programme was used for

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fitting the impedance/admittance spectra to the electrical circuit models.

3. Results and discussion

Fig. 1 shows a series of Nyquist plots obtained at selective potentials from 0.18 to 0.7 V for BF_4 doped PANI films. Since the film charge and the impedance response remain unchanged with time of experimentation, including the use of multiple scans, the film prepared has been concluded to be stable. Potentials greater than 0.7 V were not investigated, as it is expected to lead to loss of charge and also of some film capacitance due to over oxidation/degradation process [14]. Further, it can be seen that PANI film changes from being much more resistive materials at low potentials to a very low resistance and high capacitance one at higher potentials, consistence with numerous previously published results [15,16]. In the fully reduced form of PANI, at 0.0 V, the Nyquist plot/Fig. 2 shows the presence of essentially only a single semicircle (i.e.) only one time constant with the extrapolated diameter of the circle on the real impedance axis being indicative of a relatively high resistant system. This is realized for all acids and a representative example

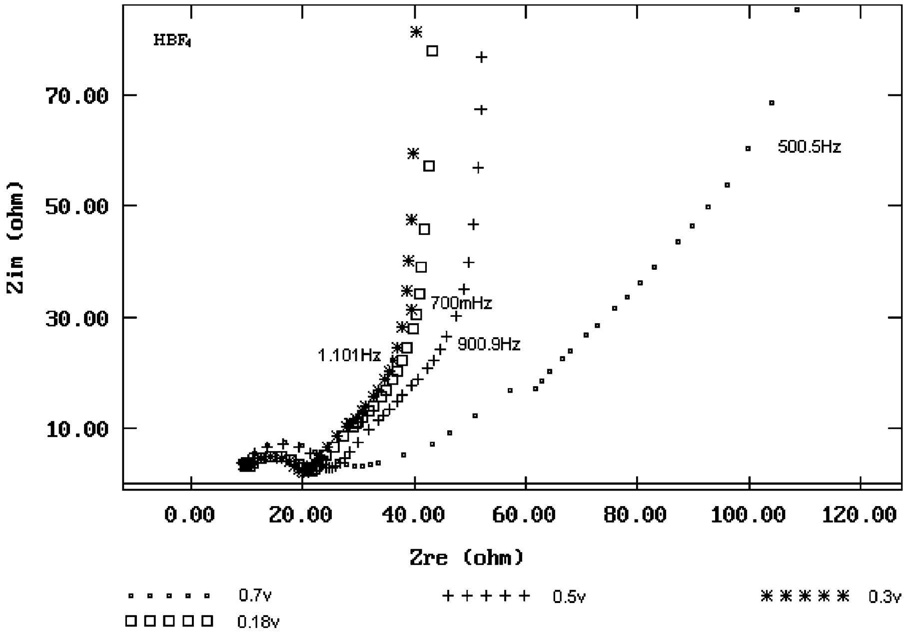

Fig. 1. Complex plane impedance plots of thin film PANI electrode at potentials ranging from 0.18 to 0.7 V doped with 2 M HBF_4 having a thickness of 159 nm.

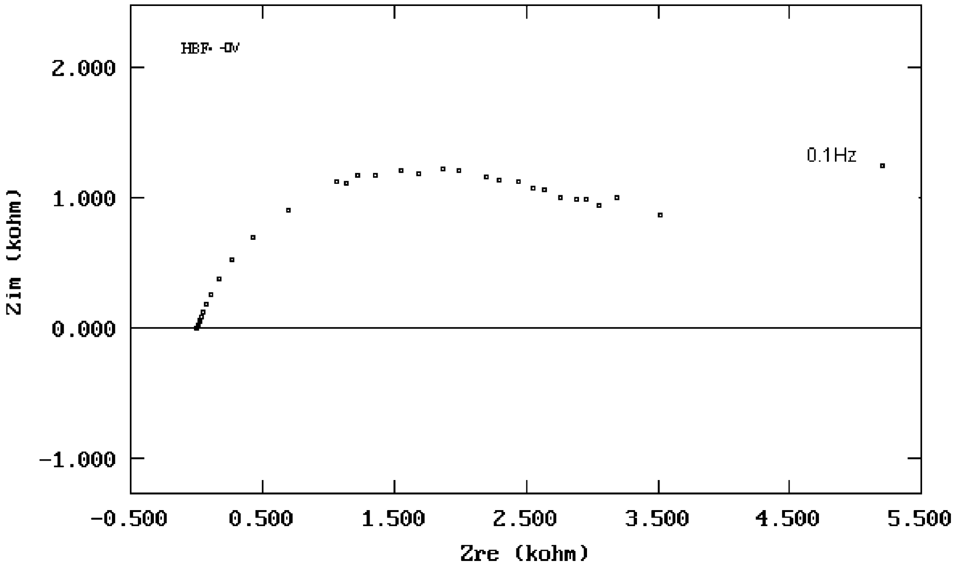

Fig. 2. Complex plane impedance plots of thin film PANI electrode at 0 V doped with 2 M HBF_4 for 159 nm thickness.

is shown in this Fig. 1 to substantiate the potential dependant a.c. impedance response under the conditions employed in this investigation. On the other hand, in the conducting form that appears in the potential window between 0.18 and 0.7 V, the large psuedocapacitance of the film is revealed by the vertical segment in the Nyquist plot, with the extrapolated impedance on the real axis yielding very low film (and solution) resistance under these conditions. This behavior of conducting PANI is primarily responsible for considering this polymer as an attractive and potential candidate for electrochemical capacitor fabrication.

The exchange current density determined [17] from the a.c. impedance responses of PANI film at different potentials and for various acids is shown in Table 1. The values indicate that the films are conducting and facilitate easy ion transport across the films of various thickness. Large capacitances exhibited by PANI films for various acids are attributable to the double layer capacitance and psuedocapacitance originating from the redox process of the polymer film. The two contributions are referred as [18] the fast and the slow charging of polymer film electrode, respectively. The former determines the high frequency (HF), the later the low frequency (LF) response of the conducting PANI film to the small amplitude sinusoidal electrical perturbations. Detail analysis of the impedance spectra in terms of the frequency independent parameter has shown other capacitive components of importance for the electrode response. The analysis of complex electrode impedance function has enabled the evolution of the following relations for the determination of C_{dl} and C_{o} (double layer and redox capacitance, respectively), these impedance response have been utilized to determine the double layer capacitance (C_{dl}) and redox capacitance (C_{o}) based on the well-known complex electrode impedance function [18], which on deducing for higher frequency and lower frequency gives the following expression:

$$Z(j\omega)_{\mathrm{hf}} = R_{\mathrm{hf}} + \frac{1}{J\omega C_{\mathrm{dl}}}$$

and

$$Z(j\omega)_{\mathrm{lf}} = R_{\mathrm{lf}} + \frac{1}{J\omega C_{\mathrm{o}}}$$

where Z is the impedance, j the complex number (-1), ω the angular frequency, R_{hf} the high frequency resistance, C_{dl} the double layer capacitance, R_{lf} the low frequency resistance, and C_{o} the redox capacitance.

The value of C_{dl}, the double layer capacitance, has been determined from the HF region of the impedance spectrum while C_{o}, the redox capacitance, has been determined from the LF region of the impedance spectrum.

These two equations describe the limiting behavior of the polymer film electrode in terms of frequency independent resistances and capacitances. As these parameters are functions of the redox state of the polymer (that is controlled by d.c. potential applied to the polymer electrode),

Table 1
Exchange current density for different acids for different thickness at various potentials

Potential (V)	Thickness (nm)	H_2SO_4, I_o ($A\,cm^{-2}$)	HCl, I_o ($A\,cm^{-2}$)	HBF_4, I_o ($A\,cm^{-2}$)	$HClO_4$, I_o ($A\,cm^{-2}$)
0	119	5.98E − 4	1.7E − 4	5.9E − 5	6.25E − 5
0.18		9.52E − 4	5.6E − 4	3.55E − 4	7.36E − 5
0.3		8.54E − 4	4.4E − 4	4.17E − 4	2.21E − 4
0.5		1.03E − 3	4.4E − 4	4.72E − 4	2.43E − 4
0.7		1.98E − 3	1.2E − 3	4.82E − 4	3.20E − 4
0	159	2.02E − 3	8.30E − 5	2.95E − 4	7.70E − 5
0.18		3.84E − 3	1.94E − 3	8.03E − 4	1.12E − 4
0.3		3.54E − 3	4.88E − 4	8.03E − 4	4.17E − 4
0.5		4.01E − 3	9.66E − 4	8.03E − 4	2.56E − 4
0.7		4.44E − 3	2.12E − 3	9.2E − 4	6.57E − 4
0	199	2.14E − 3	2.57E − 4	2.02E − 3	6.85E − 5
0.18		4.15E − 3	3.20E − 3	3.84E − 3	2.73E − 4
0.3		3.75E − 3	2.07E − 3	3.54E − 3	2.43E − 4
0.5		4.24E − 3	2.21E − 3	4.01E − 3	2.93E − 4
0.7		9.6E − 3	2.54E − 3	4.44E − 3	3.90E − 4
0	399	1.23E − 2	1.19E − 3	4.71E − 4	2.10E − 4
0.18		2.14E − 2	7.30E − 3	4.76E − 4	2.49E − 4
0.3		1.93E − 2	6.76E − 3	6.79E − 4	1.92E − 4
0.5		2.20E − 2	6.94E − 3	6.26E − 4	3.29E − 4
0.7		4.80E − 2	8.21E − 3	7.11E − 4	4.43E − 4
0	1000	2.42E − 2	1.95E − 3	1.05E − 3	1.95E − 3
0.18		4.40E − 2	4.20E − 3	1.31E − 3	4.42E − 3
0.3		4.60E − 2	3.75E − 3	1.13E − 3	3.75E − 3
0.5		4.60E − 2	3.75E − 3	1.36E − 3	3.75E − 3
0.7		5.74E − 2	4.40E − 3	2.99E − 3	4.40E − 3

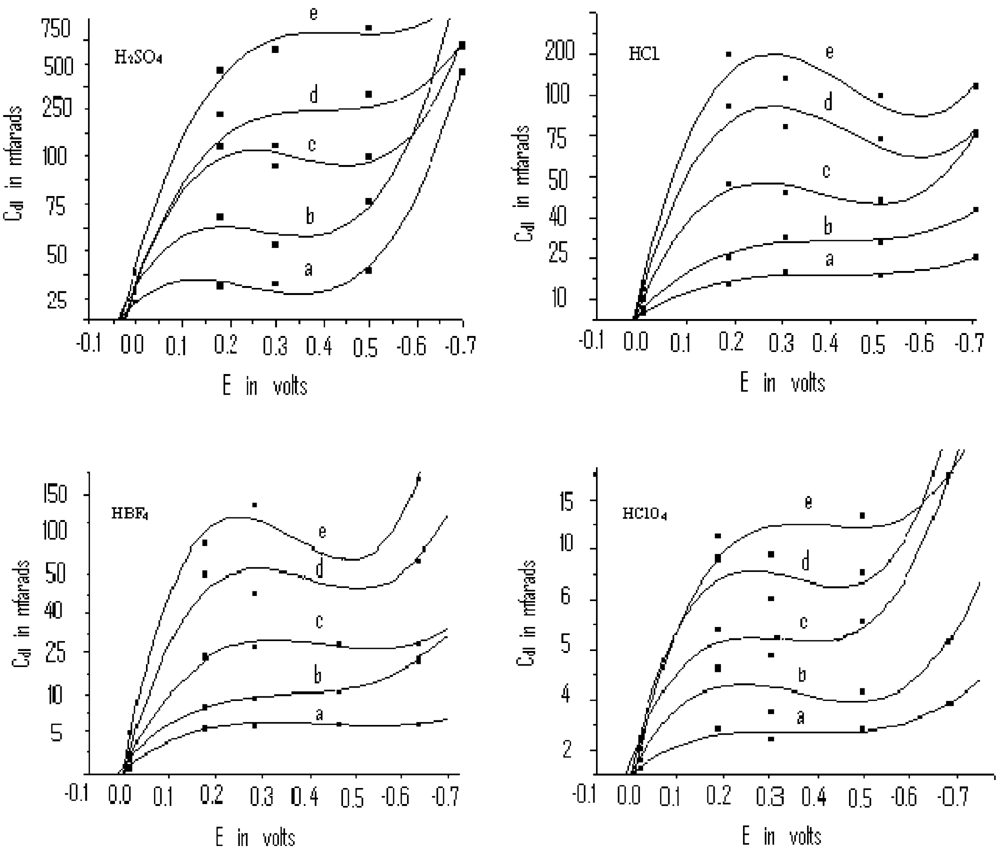

Fig. 3. Dependence of C_{dl} with potential for various thicknesses: (a) 119, (b) 159, (c) 199, (d) 399, and (e) 1000 nm for various acids.

the contributions of these two capacitive components over conducting redox potential window have been determined and found to follow a set pattern.

Fig. 3 shows a sigmoidal dependence of the double layer capacitance C_{dl} on d.c. potential for the electroactive polyaniline/electrolyte interface measured with different acids (H_2SO_4, HCl, HBF_4 and $HClO_4$). This observation conforms to the previously observed trend of PANI film [19]. The important effect demonstrated here is the effect of thickness of the film and the nature of acid dopant employed which has a profound influence on the C_{dl} values. The increase in thickness of PANI film with each counter ion derived from acid has facilitated progressively higher C_{dl} values while indicating an increase in conductivity range, and a higher doping level. These observations are in agreement with the reported trend of thin PANI film [20].

As is seen here, for each counter ion derived from acid, all the PANI films shows increasing C_{dl} values as the potential region shifts from 0 to 0.7 V. At the first redox potential region namely 0.18 V, the jump to the higher value is spontaneous. The degree of spontaneity is seen to be thickness dependant in all the cases and progressive in nature. This trend is due to the increase in C_{dl} value at all the potentials beyond 0.18 V and levels off up to 0.5–0.55 in almost all cases which again tends to increase. The higher C_{dl} values at this redox potential and beyond this point occurs due to the fact that the microscopic interface between polymer chain and ionic solution generates a huge area for electrical double layer [21–24]. The apparent further increasing trend of C_{dl} value beyond 0.5–0.7 V in all the cases is attributable to second redox peak that is normally realizable with higher thickness of PANI film. Since the present study has been confined to thin films (i.e.) up to 1 μm, this apparent increase in trend is not analyzed at this stage. While the pattern of rise in C_{dl} values in all the acid medium studied for PANI film is similar with respect to thickness and increase in potential window, the individual values of C_{dl} determined vary vastly. The highest value of C_{dl} obtained at 0.7 V has been realized for H_2SO_4 grown PANI film (665 mf cm^{-2}), while the lower values of C_{dl} has been observed for $HClO_4$ (13 mf cm^{-2}). This dependence is attributed to change in the double layer structure as a result of the changes in the redox process of polymer facilitating changes in the characteristics of polymer/electrolyte junction due to reduction/oxidation. This effect is more pronounced at higher potential region wherein the PANI exists in oxidized form. Hence, the C_{dl} value of the PANI film at 0 V corresponding to reduced state has a lower value.

In a similar fashion, Fig. 4 shows the sigmoidal dependence of C_o on d.c. potential for the electroactive

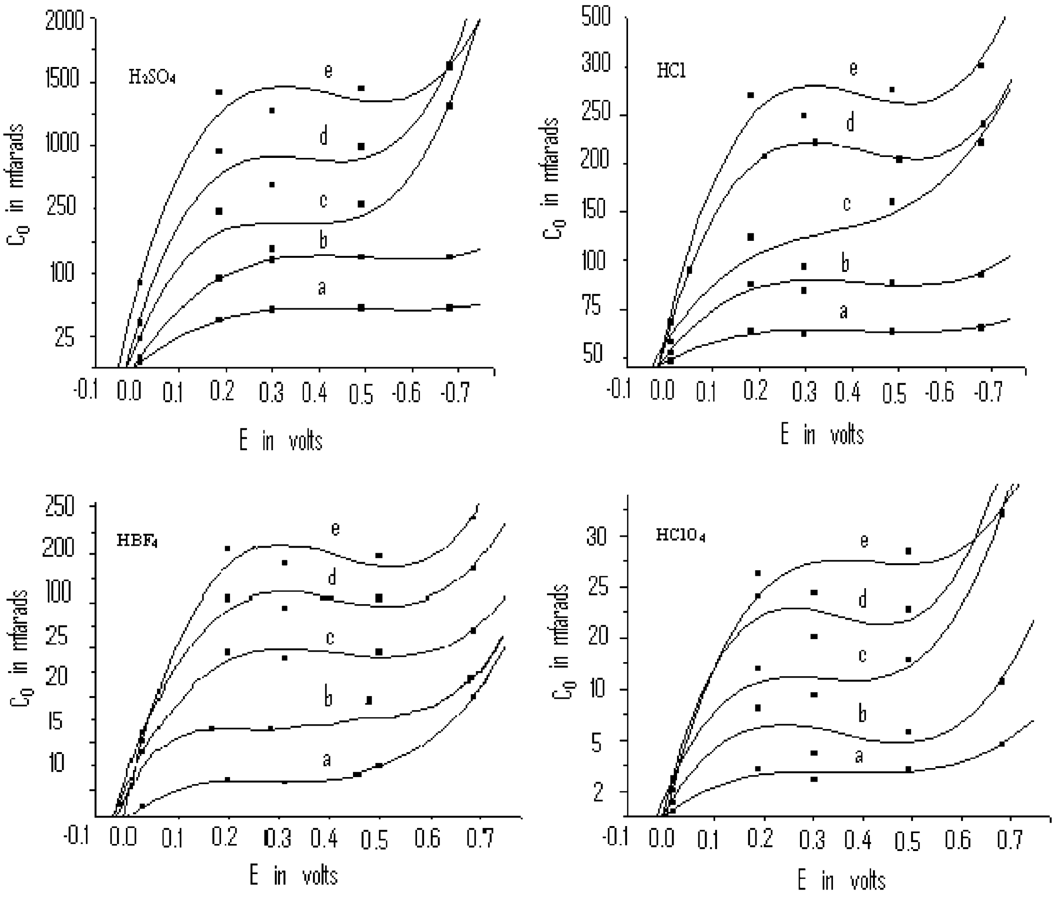

Fig. 4. Dependence of C_o with potential for various thikcknesses: (a) 119, (b) 159, (c) 199, (d) 399, and (e) 1000 nm for various acids.

polymer/electrolyte measured with different acids (H_2SO_4, HCl, HBF_4 and $HClO_4$). In the potential window 0.18–0.5 V corresponding to the conducting form of PANI, the value of C_o for each thickness is higher than the corresponding C_{dl} values shown in Fig. 3. No consideration on the conductivity mechanism in the polymer is taken into consideration and it is based on either delocalized electrons or the electron hopping mechanism. The pattern of increase in the determined C_o values follows the same style as that of C_{dl} shown in Fig. 3 with respect to thickness and potential window of the medium. The order of the capacitance value with respect to the acidic medium also follow the same order (i.e.) $H_2SO_4 > HCl > HBF_4 > HClO_4$. This trend can be supported by the fact that the ionic radii of the counter ion derivable from the set of acids are 1.74, 1.81, 2.26 and 2.36 Å [25]. This increase in ionic radii is proportional to the decrease in order of diffusion coefficient values [26]. The higher diffusion coefficients facilitates higher level of ion insertion/extraction in PANI film. In addition to the sigmoidal dependence of two different capacitance over d.c. potential, the value of C_{dl} and C_o have been deduced for various thickness/d.c. potential as shown in Table 2. The thickness of the polymer film also influences the both C_{dl} and C_o values towards increasing order, which is due to increase in, surface area. This is understandable by the fact that the pore size is expected to increase if one assumes a cylindrical size for the pore, which ultimately facilitate the higher surface area. This is well pronounced in the redox active region at above 0.18 V.

The higher surface area predicted is justifiable in comparison with already published data of SEM photomicrograph [27]. Accordingly, PANI film prepared under similar condition in sulfuric acid showed a granular structure of high porosity, which provides easy accessibility to the electrolyte. On the other hand, the PANI film prepared in $HClO_4$ showed a rather compact structure on which bunch of fibers are superimposed. The compact layer formed during potentiodynamic polymerization has been found lesser accessibility to the electrolyte. The data presented in Table 2 for all the acids conforms to this known documented information. Further, the values of the C_T obtained in all the acids are in close agreement with values reported in the published literature [28,29]. Thus these values while conforming to the known source, provides categorization into two different capacitative components as determined by the a.c. impedance spectroscopy. Thus it is seen that the higher values of measured capacitance (i.e.) C_T is attributed to the parallel combination of C_{dl} and C_o, the value of C_{dl} is far less than C_o. The

Table 2
Determination of C_{dl} and C_{o} of polyaniline film electrodes in different acids for different thicknesses

Potential (V)	Thickness (nm)	H_2SO_4		HCl		HBF_4		$HClO_4$	
		C_{dl} (mF cm^{-2})	C_{o} (mF cm^{-2})	C_{dl} (mF cm^{-2})	C_{o} (mF cm^{-2})	C_{dl} (mF cm^{-2})	C_{o} (mF cm^{-2})	C_{dl} (mF cm^{-2})	C_{o} (mF cm^{-2})
0	119	5.15	11.8	3.81	–	1.45	4.1	0.065	0.6
0.18		7.75	21.75	11.9	39	4.7	8.62	0.176	1.6
0.3		6.75	19.45	15.2	36.5	5	9.95	0.195	1.05
0.5		8.3	22.7	14.3	40.2	5.1	12.4	0.755	1.43
0.7		16.5	36.45	19.45	41.45	5.1	12.4	0.515	2.05
0	159	16.9	34	10.43	15.4	3.92	–	0.129	1.09
0.18		30.2	65.5	20.2	50	9.93	14.0	1.12	1.53
0.3		37.1	60.5	21	53.8	10.9	12.9	0.89	1.42
0.5		39	71.65	21.25	69	9.65	14.5	1.03	1.88
0.7		41.9	91.7	25.6	72	–	16.4	1.85	1.90
0	199	22.45	40	15.35	49.5	4.35	11.7	0.58	2.43
0.18		58	78	22.2	70	10.7	17.5	1.14	2.48
0.3		53.1	72	22.4	–	12.8	17.0	1.15	2.9
0.5		55.5	84.1	23	77	11.8	17.5	1.17	2.94
0.7		83.5	188	25.65	98.5	14.9	20.23	1.56	2.95
0	399	80.2	286	20	–	17.1	40.25	2.02	3.51
0.18		202	464	24.05	79	40	77.5	2.25	5.4
0.3		181	419	23	53	37.65	71.5	2.25	6.6
0.5		217	472	25.05	96	39.8	84	2.6	9.14
0.7		253	–	30.05	217	41.6	91	4.36	9.15
0	1000	420	1015	178.5	–	105	185	8.2	0.91
0.18		437	1044.5	178	188	126	224	9.04	17.1
0.3		439.9	1044	162	168.5	120.5	210	8.2	19.5
0.5		454	1045	170	185	138	208.5	9.65	22.9
0.7		665	1355	255	265	145	215.5	13	28.6

C_{o} is the bulk parameter of the film and a reflection of the actual ion insertion/extraction process in the PANI film.

Among these two capacitive components the C_{o} gains more importance, as it is dependant on redox active character of polymer film. When the modulation of redox character of any electroactive polymer is possible, it is intriguing to explore the possibility of increasing the contribution of this capacitive component to the overall capacitance of the chosen, this approach will provide screening of all possible combinations of redox chemistry possible with conducting polymer films, thereby providing redox activity-capacitance correlation through various preparative options available. The role of redox capacitance to the overall capacitance of PANI electrode is best illustrated in Fig. 5, wherein the C_{o} is compared with total capacitance C_{T} measured in this investigation. In all the acids used the C_{o} values are distinctly higher in redox active region when compared to C_{dl} values.

The importance of C_{o} to overall C_{T} is further demonstrated by identifying the frequency at which the "charge saturation point" occur in each acid for the PANI film electrode using Gabrielli model [30] proposed for redox active substance. According to this model, the impedance response of an electroactive polymer film can be theoretically categorized into three regions namely charge transfer, diffusion charge transport and charge saturation. The latter region namely "charge saturation" occurs at LF region wherein the tendency to form straight lines to form angles with the real axis somewhat lower than 90° has been shown to be the capacitive behavior of the resultant polymer film. The frequency at which the formation of straight lines in a.c. impedance experimental region can thus be called "charge saturation point" or otherwise called capacitive straight line [31]. This "charge saturation point" referred as capacitive straight line has been determined from the Nyquist plots obtained for all the acids at different potential and the same is shown in Table 3. It can be seen that at the redox active region the "charge saturation" occurs uniformly for all the acids used with only difference being its occurrence at various frequency for various acids. This is understandable due to differences in electrical response of a.c. signal with respect to chemical feature in film. The chemical features of the film originates primarily from the nature of counter ions that is hold in PANI film which in turn follows various diffusional charge transport at varied potential window by virtue of the doping–dedoping process. Further, these counter ions have varied diffusion coefficients and accordingly the response of a.c. impedance spectra is bound to change. This is well reflected in the varied values of "charge saturation point" at different potential for all the counter ions studied. This is further supported by the fact that the values of C_{o}

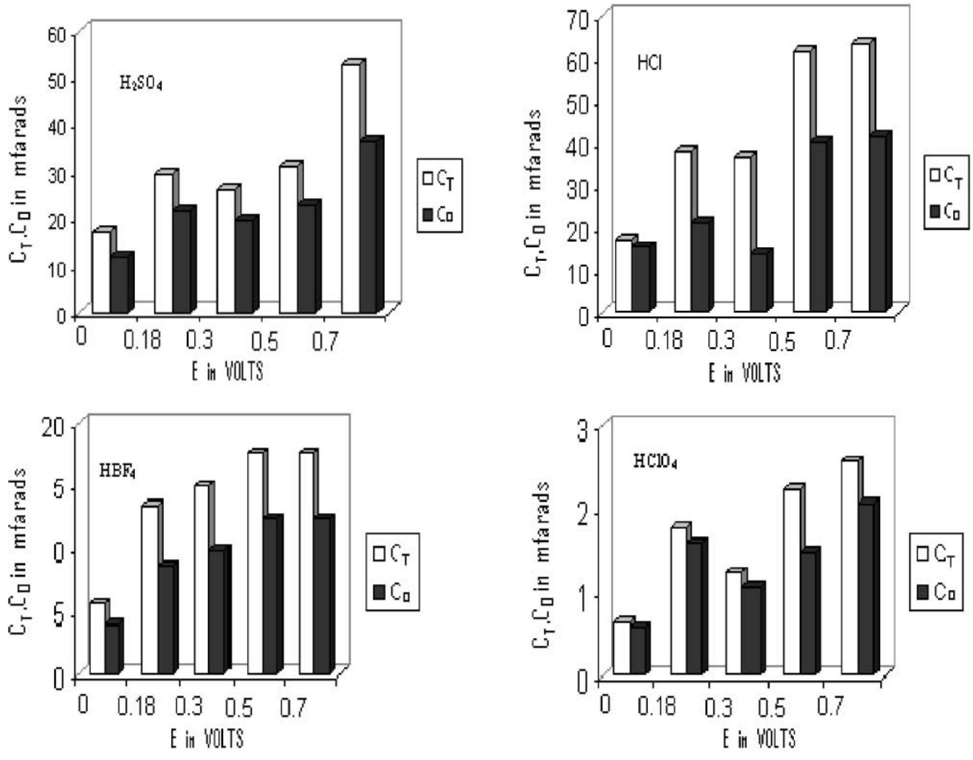

Fig. 5. Contribution of C_o over C_T at various potentials for 119 nm thickness.

(so also C_{dl}) (vide Table 3) with respect to C_T measured in every case varies and follows the established pattern [32,33].

Thus this study provides the importance of diagnosing two different capacitive components of conducting polymer electrodes while screening this class of electrodes for electrochemical capacitor fabrication. The use of a.c. impedance spectroscopy has been utilized to quantify this and for the first time the determination of "charge saturation point" with respect to counter ions of PANI film has been used to pinpoint the occurrence of beginning capacitive straight line, a diagnostic proof of capacitive behavior of redox polymer film. The quantification of these parameters, assumes relevance when one attempts to modify the conducting polymer electrodes towards fixing predetermined capacitance value in custom making the desired capacitor.

Table 3
Charge saturation point for various acids at 1000 nm thickness

S.No.	Dopants	Potential (V)	Charge saturation point (Hz)
1	H_2SO_4	0	8.303
2		0.18	10
3		0.3	10
4		0.5	10
5		0.7	6.707
1	HCl	0	–
2		0.18	398.1
3		0.3	398.1
4		0.5	100.01
5		0.7	100.01
1	HBF_4	0	9.71
2		0.18	10
3		0.3	10
4		0.5	8.308
5		0.7	6.707
1	$HClO_4$	0	–
2		0.18	8.308
3		0.3	39.81
4		0.5	39.81
5		0.7	25.12

4. Conclusion

The a.c. impedance technique has been used to screen polyaniline film doped with different counter ions derived from various acids: in terms of the contributions of double layer and redox capacitance to the overall capacitance of the polymer film electrode. The thickness and nature of counter ions have been found to have profound influence over both the capacitive components. This effect has been analyzed with respect to electroactive potential-window of polyaniline and it indicates the possibility of modulating the capacitance through preparative methodologies of conducting polymer film. The determination of "charge saturation point" for PANI films enabled the pinpointing of the occurrence of frequency dependant capacitive behavior.

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