

Impedance Study of Drinking Water and Tastants using Conducting Polymer and Metal Electrodes

Mopsy Dhiman, Pawan Kapur, Abhijit Ganguli, Madan Lal Singla

Abstract- In this study the sensing capabilities of a combination of metals and conducting polymer electrodes for drinking water and dissolved tastants using an AC-impedance mode in frequency range 10^2 to 10^5 Hz at 0.1 V potential has been carried out. Classification of seven different bottled and municipal drinking water samples along with various tastants dissolved in DI water (DI water) for KCl (5mM) (salty), HCl (5 mM) (sour) quinine (0.1 mM) (bitter), sucrose (5 mM) (sweet), black tea liquor, black tea liquor with sucrose (2% sugar solution), and a bottle of "packed" orange juice has been made using six different working electrodes in a multi electrode setup using PCA. Working electrodes of Platinum (Pt), Gold (Au), Silver (Ag), Glassy Carbon (GC) and conducting polymer electrodes of Polyaniline (PANI) and Polypyrrole (PPY) grown on an ITO surface potentiostatically have been deployed in a three electrode set up. The impedance response of these water samples using number of working electrodes shows a decrease in the real and imaginary impedance values presented on nyquist plots depending upon the nature of the electrode and amount of dissolved salts present in water/tastants. The different sensing surfaces allowed a high cross-selectivity in response to the same analyte. From PCA plots it was possible to classify drinking water in 3-4 classes using conducting polymer electrodes; however tastants were well separated from the PCA plots employing the impedance data of both conducting polymer and metal electrodes.

Keywords: - Sensing electrodes, AC-impedance, Principal component analysis, Drinking water, tastants, conducting polymers.

I. INTRODUCTION

Water is an essential precursor to the discovery of life [1]. It is one of the abundantly available resources in nature and is important for animal and plant life [2]. The use of artificial sensors for evaluating water quality for drinking purpose and tastants in beverages is largely increasing. Impedance study responds to the compounds responsible for basic tastes in much the same way as the biological system and may detect differences between beverages having similar flavours. For instance, some of them can distinguish between different brands of mineral water or between different brands of wine, in addition to detecting ionic metals in water. Different methods have been used in these studies for substances ensuring sweetness, saltiness, sourness, bitterness and umami by potentiometry [3-6], voltammetry [7-11] and admittance measurement [12]. Recently, the interest to learn more about AC-impedance technique has rapidly grown in the bio-electrochemistry for sensor studies. Impedance measurement is the study of conductivity and impedance is a numerical expression of the ability of an aqueous solution to carry electric current.

Impedance depends on the presence of dissolved ions, the electrochemical nature of the sample [13-15],

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Temperature and the type of electrodes, polarization behavior on the electrode surface [16-18] and the thickness of the doped polymer film on the electrode surface [19-20]. The AC-impedance technique provides information about physical and chemical processes occurring on electrode surfaces. Riul et al developed an artificial taste sensor based on LB films of conducting polymers [12]. Robberg and Paasc analyzed the porosity nature of PANI films based on redox processes [20]. Zic has discussed the role of polymer thickness in impedance studies [19].

Ragheb and Geddes determined the polarization impedances of different metal electrodes (e.g., stainless steel, Pt, silver, MP35N, palladium, aluminum, rhodium and copper electrodes) [21] and Krantz-Rulcker et al used six working electrodes namely, Au, Iridium, Palladium, Pt, Rhenium and Rhodium to analyze citric juice, tea, and milk, and to monitor potable water using voltammetry [11]. Viatcheslav and Sarit presented the principle and theoretical basis of the application of EIS to the study of ion transport and partitioning in thin film, as well as in solid electrodes exposed to an electrolyte solution [22]. The reduction and oxidation states occurring in the solution are due to the charge transfer of anions from the electrolyte in metal electrode surface. In the case of conducting polymers, it is across the pore surface of the film or due to proton release from the polymer [23]. Laboratory conductivity measurement is used to assess the degree of mineralization of distilled water and DI water, which are used to evaluate variations in dissolved mineral concentrations of raw water and wastewater [24]. Taylor and Mc Donald described an equivalent circuit in the sensing system to understand the theoretical phenomenon behind impedance measurement studies [25].

In this study, we analyzed the impedance behavior of drinking water and tastants at a constant voltage of 0.1 V in the frequency range from 10^2 to 10^5 Hz using a combination of electrodes. For this different samples of bottled drinking water, groundwater were used aside from different tastants such as KCl (salty), quinine (bitter), HCl (sour) and sucrose (sweet) in deionized (DI) water, black tea and a liquor of black tea with sucrose. The metal electrode surface area was kept constant for all the measurements. The impedance measurements of ITO-Polyaniline (ITO-PANI), ITO-Polypyrrole (ITO-PPY) conducting polymer electrodes were also compared with metal electrodes. In all the electrodes the average impedances of each electrode after repeated measurements of the samples over a period of 90 days were taken into consideration and used for the AC-impedance study and principal component analysis (PCA).



II. Experimental Section Materials and method (Chemicals used)

Drinking water supplied from the municipality of Chandigarh (India) and groundwater (hand pump water) samples from the same area together with samples of bottled drinking water by 5 different companies labelled A (treated using reverse osmosis and ozone), B (treated using reverse osmosis), C (ozonized with added minerals), D (treated with ozone), E (treated by reverse osmosis and ozonized with added minerals, procured from local market of Chandigarh (India)). All the basic tastants were prepared in the laboratory using AR analytical grade chemicals, KCl (5-50 mM Cl⁻) HCl (5 mM) (from Loba Chemie, India), quinine 0.1 mM (Fluka), sucrose 5 mM, 5% black tea solutions prepared by dipping a 5 gm of (Brook Bond-Taj Mahal) tea bag in 100 ml of DI water, and another tea solution prepared by adding 1 gm of sucrose to 50 ml of black tea and a pack of "packed" orange juice (Minute Maid from Coca-Cola). The chemicals used for the preparation of conducting polymer sensors are aniline and pyrrole (Spectrochem Pvt Ltd. India), LiClO₄ (Alfa Aesar), H₂SO₄ (Ranbaxy, India), and Indium Tin Oxide glass plates.

III. ELECTROCHEMICAL EQUIPMENT

CHI Instruments Electrochemical workstation 660C (Austin, TX, USA) was used for the impedance study. All the AC-impedance experiments were carried out at 20±20C using a single compartment 3 electrode cell. Pt, Au, GC, and Ag (Supplied by CHI Instruments) were used as working electrodes; ITO-PANI and ITO-PPY working electrodes were grown potentiostatically. Pt wire as the counter electrode and Ag/AgCl (4M KCl) as the reference electrode were used. The AC-impedance parameters were +0.1 V potential for 60 s at an amplitude of 0.005 V with a frequency range from 10² to 10⁵ Hz.

IV. METAL ELECTRODE POLISHING AND ELECTRO POLYMERIZATION OF CONDUCTING POLYMERS AT ITO COATED GLASS SURFACE

All the four metal electrodes (Pt, Au, glassy carbon, and Ag) were polished to obtain a smooth surface with alumina powder (Al₂O₃, CH Instruments, Inc, USA) of particle sizes of 1, 0.3, and 0.05 μm and washed before use. PANI and PPY films were deposited on the ITO surface (0.8 cm²) by the electro polymerization of the respective monomers in a glass cell having a three electrode ITO coated glass as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode. For the ITO-PPY electrode 0.1 ml of pyrrole monomer and 10 ml of 0.2M LiClO₄ were taken in the glass cell and a film was grown potentiostatically at +1 V for 30s. Similarly PANI films were grown on an ITO surface using 0.5 ml of aniline in 10 ml of 0.2 M H₂SO₄ at +1.2 V for 60s by the potentiostatic method. Each ITO-polymer film electrode was washed with DI water 2-3 times dried and kept in a dessicator before and after use. Each polymer electrode was observed 10 times [29].

V. PRINCIPAL COMPONENT ANALYSIS OF WATER AND TASTANTS

Quality assessment studies of seven types of drinking water and different tastants were carried out by PCA.

PCA for Drinking water

I. A set with four electrodes (Pt, Au, Ag, glassy carbon), a set with two polymer electrodes (ITO-PANI, ITO-PPY) and a set with all the six electrodes (Pt, Au, Ag, glassy carbon, ITO-PANI, and ITO-PPY) for drinking water.

PCA for Tastants

II. PCA plot- A having six electrodes with tastants.

VI. RESULTS AND DISCUSSION

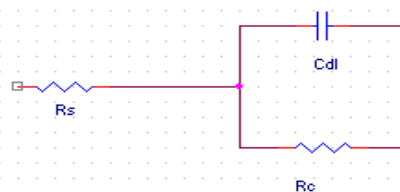
Electrochemical impedance was measured by applying an AC potential to an electrochemical cell containing the sample solution and measuring the current through the cell using small excitation signals.

VII. EQUIVALENT CIRCUIT / RANDLE'S MODEL

The complex plane plot or Nyquist plot obtained by impedance study is due to the Randle's equivalent circuits, where Cdl is the double-layer capacitance, Rs is the bulk sample solution resistance, Rc is the charge-transfer resistance associated with the double layer [Fig.1 (a), Fig.1 (b) and Fig. 1(c)].

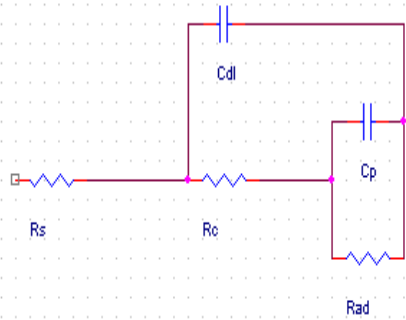


Fig.1 (a): Randle's model showing Solution resistance Rs, Double layer resistance Cdl, Charge transfer or polarization resistance Rc



Randle's Equivalent Circuit

Fig.1 (b): Randle's Equivalent circuit



Equivalent Circuit due to adsorption

Fig.1(c): An equivalent circuit for PANI and PPY

The circuit components represent the processes contributing to the overall impedance of the system. These circuits are used mainly for the analysis of impedance data [12]. A Nyquist plot for a typical Randle's cell is always semicircular. The solution resistance can be found on a real axis at a high-frequency intercept [Fig.1 (d)].

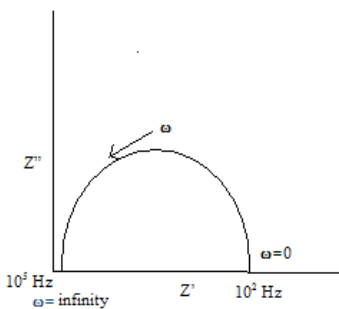


Fig.1 (d): Nyquist plot diagram in the solution resistance with frequency range 10^2 to 10^5 Hz where $\omega=0$ at minimum impedance and $\omega=\infty$ at higher impedance measurements

This intercept near the origin of the plot and the real axis value on the other side is the sum of polarization resistance, and solution resistance and the diameter is equal to the polarization resistance. In impedance techniques, the practical difficulties lie in the choice of an appropriate equivalent circuit and an accurate electrical fitting procedure [26] and in some aspects of the impedance of conducting polymer within high-frequency limits is the correct assignment of the ohmic resistivities obtained from the fits [20].

Impedance study of DI water samples

The response of four electrodes (Au, Pt, Ag and glassy carbon) and two conducting polymer electrodes (ITO-PANI, and ITO-PPY) for DI water in the frequency range of 10^2 to

10^5 Hz with a potential of 0.1 V are given in Fig. 2 (a) and Fig.2 (b), respectively.

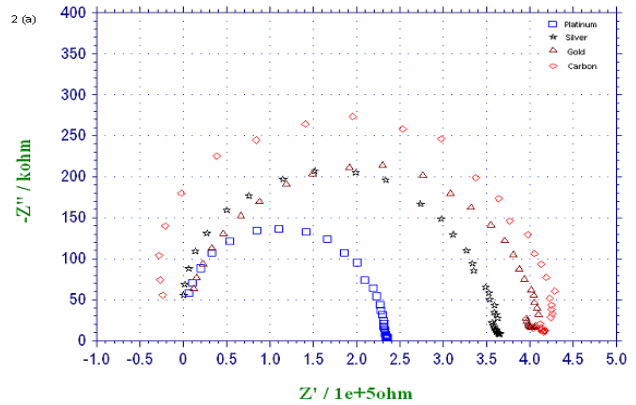


Fig.2 (a): Nyquist plot for DI water using four metal electrodes (Pt, Ag, Au, Glassy Carbon)

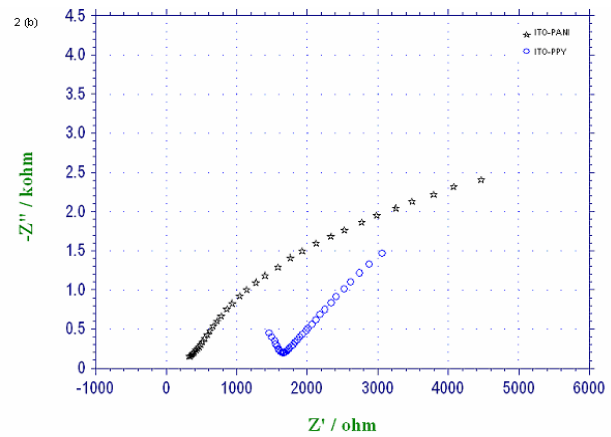


Fig.2 (b): Nyquist plot for conducting polymer electrodes ITO-PANI and ITO-PPY for DI water

In these impedance plots, each electrode surface represents the response for DI water. The complex plane plot of impedance behavior in Fig.2 (a) shows a semicircle. This half circle is a characteristic of a single time constant, although the electrical impedance plots often contain several time constants. The single time constant may be due to the DI water being a poor conducting solution resulting in higher impedances, forming a semicircle. The impedance plot clearly shows that the Pt electrode is least polarized in comparison to Au and silver, whereas the GC electrode is highly polarized. The behavior of the PPY and PANI electrodes has been found to be 45° oblique line which may be due the conducting nature of the polymer. The resistance of the polymer surface is negligible in comparison to the electrolyte resistance. Thus, the polymer is in its oxidized state and the impedance is equal to the electrolyte between the working and reference electrodes [20, 26-28]. The average impedances observed with these 6 electrodes are given in Fig. 3, which shows that the GC and Au electrodes are highly sensitive.



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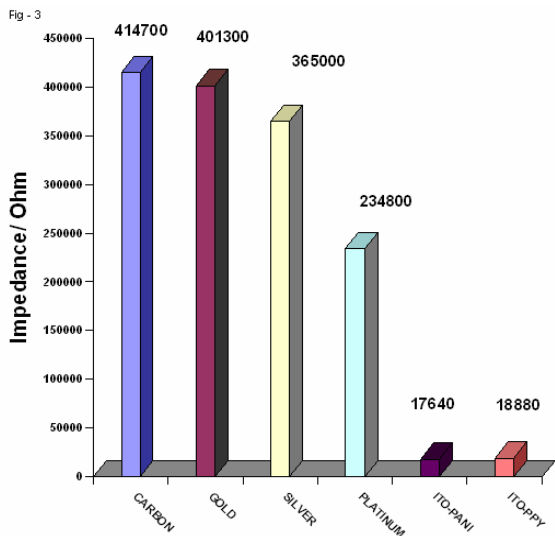


Fig.3: AC-impedance of DI water with impedance values from six different electrodes GC, Au, Ag, Pt, ITO-PANI, ITO-PPY (Left to Right)

VIII. IMPEDANCE STUDY OF SEVEN DIFFERENT DRINKING WATER SAMPLES

The AC-impedance of five bottled water samples, municipal water, and groundwater are represented in Fig.4 using all the six working electrodes.

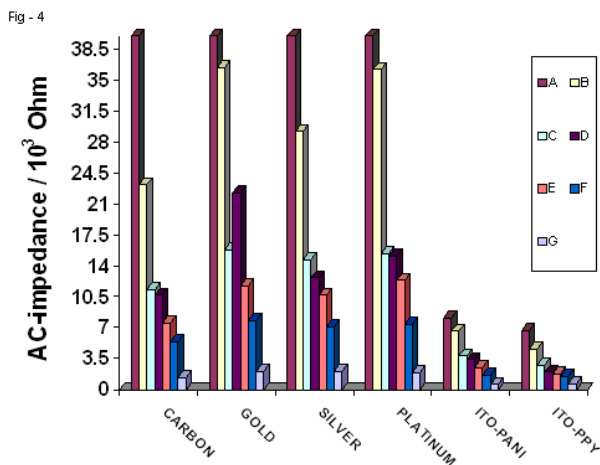


Fig.4: AC-impedance of water samples: A (Aquaafina) B (Kinley) C (Bisleri) D (Paras) E (Equal) F (Municipal supply of drinking water from Chandigarh) G (Ground water from hand pump)

Sample A shows the higher impedance values with the three metal electrodes, GC electrode as well as with conducting polymer electrodes, indicating that this water may contain fewer dissolved ions, hence shows a flattened circle on a complex plane plot. Sample B represents almost similar values with no significant impedance changes in Au or Pt, whereas the impedance of the Ag and GC electrodes are of the order of 75% and 50% approximately to that of the Au and Pt electrodes. The B, C, D, E, and other drinking and groundwater samples have lower impedance output for GC, Ag, Au, and Pt electrodes.

The impedance behavior of Au electrode with sample D shows somewhat higher impedance values in comparison to other metal electrodes, while conducting polymer electrodes

have low impedance output. Thus impedance data explains some relation between Au electrode and Sample D at higher impedance which may be due to dissolved minerals present that can be seen from the values of ground water sample. Impedance measurements of all the water samples on the polymer electrodes shows a charge-transfer resistance, polymer thin-film interference, the ion-diffusion co-efficient into the polymer and the redox capacitance [26], which is an important parameter of electrochemically conducting polymers. The assessment of sensors has been carried out using impedance data with the combination of sensing electrodes for different brands of drinking water in PCA. In PCA results, first principal component provides most of the information and presents the highest variance.

Fig.5 (a) represents all the four metal electrode surfaces which are able to distinguish water sample A clearly whereas B, C, D and ground water lie close to each other.

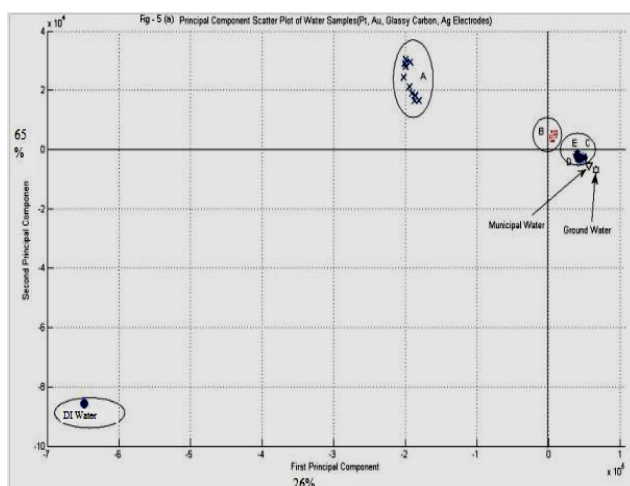


Fig.5 (a): PCA plot of water samples with four electrodes (Pt, Au, Ag and GC)

In Fig.5 (b) conducting polymer electrodes are able to clearly distinguish the bottled water in comparison to municipal and ground water which lie close to each other indicating the source of water withdrawal may be same.

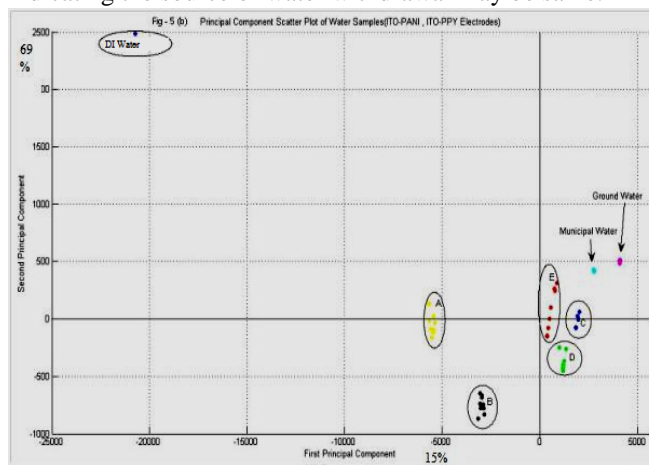


Fig.5 (b): PCA plot of water samples with conducting polymer electrodes (ITO-PANI, ITO-PPY)

Similar behavior has been observed when the PCA of six electrodes were studied together in Fig.5 (c).

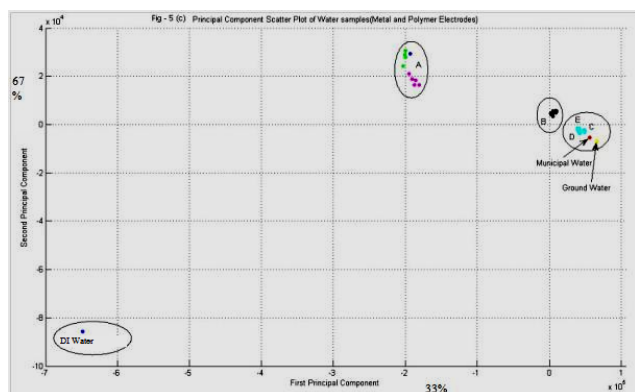


Fig.5 (c): PCA plot of water samples with the combination of metal and conducting polymer electrodes (Pt, Au, Ag, glassy carbon, ITO-PANI, ITO-PPY)

IX. PCA OF TASTANTS

Fig.6 represents PCA of various tastants having various mM concentrations in DI water. The sensing pattern of combination of electrodes clearly shows cross sensitivity at the threshold detection level for tastants, indicating specific interaction occurring between the electrode surface and the compounds dissolved in these solutions. The resulting changes may be related to the impedance behavior of these solutions in the selected frequency range. Thus, the impedance output data of the electrochemical sensor array can be used to analyze various tastants without knowing the specific compound present in it.

The PCA plot in Fig.6 clearly distinguishes between various

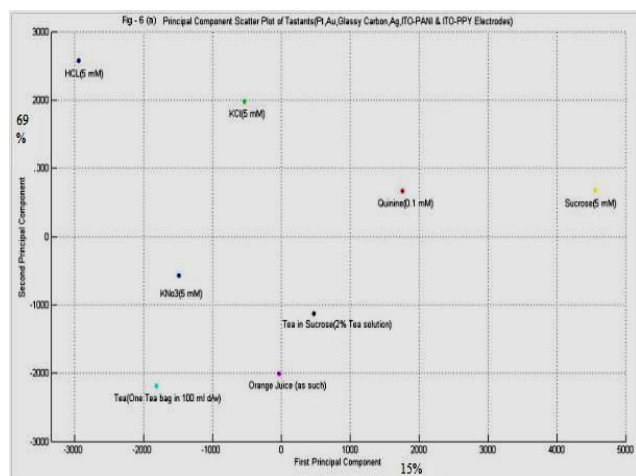


Fig.6: PCA plot for tastants using a set of six electrodes (Pt, Au, Ag, GC, ITO-PANI, ITO-PPY)

tastants i.e. sour (HCl), salty (KCl), bitter (quinine), sweet (sucrose) tastes prepared in DI water, thus indicates variable sensitivity due to the nature of tastants/cation-anion mobility towards electrode surface. The tea liquor prepared in DI water, sweet tea liquor and orange juice were also classified in the same set up. It was observed that all sweet samples lies towards the same side of the plane.

The use of conducting polymer i.e. PANI and PPY electrodes in frequency range 10^2 to 10^5 Hz was able to

classify different brands of water. The impedance behavior clearly distinguishes ground water from other water samples which may be due to the higher amount of cations and anions present in this water. Metal electrodes were not found to be much helpful in classification of different brands of water. However, six set of electrodes was able to classify threshold level tastants present in DI water. More detailed studies in impedance mode are being carried out for the further quantification of beverages and tastants quality.

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