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Influence of sodium chloride on corrosion resistance of ever silver vessels in the presence of curd rice

ABSTRACT

The present work is undertaken to investigate the corrosion resistance of ever silver in the presence of water, water+curd system, water+curd+rice system, water+curd+rice+Salt system. The corrosion resistance has been evaluated by AC impedance spectra . AC impedance spectra have been employed to investigate the corrosion resistance of ever silver electrode when it is immersed in various test solutions like water, curd, curd rice recipe, curd rice recipe with salt (sodium chloride 500 ppm). The corrosion resistance of ever silver electrode when it is immersed in various test solutions like water, water+curd, water+curd+rice and water+curd+rice+salt have been evaluated by AC impedance spectroscopy.If a protective film is formed, the charge transfer resistance increases, impedance value increases, phase angle value increases and double layer capacitance (C_{dl}) value decreases.When Ever silver electrode is immersed in water + curd rice system + 500ppmsodium chloride system, the corrosion resistance of ever silver electrode decreases. This is due to the presence of chloride ion introduced into the curd rice system. It implies that when curd rice is packed in vessels made of ever silver, we should avoid adding salt to the curd rice. It is better to keep the salt and curd rice separately. It is to be noted that this corrosion resistance is better than the corrosion resistance in water alone.

The corrosion resistance decreases in the following order:
Water + Curd + Rice system > Water + Curd + Rice + Salt system (sodium chloride 500ppm) > Water+Curd system > Water

Keywords: *corrosion resistance, ever silver, curd rice, sodium chloride, electrochemical studies*

INTRODUCTION

Corrosion of food cans is influenced by various factors. They are content of certain compounds in corrosive food products such as sulfur compounds, chloride, nitrates, etc., which are derived from canned materials or from additive compounds; acidity or pH of food products. For corrosion protection of metal cans used as food and beverage packaging, coatings based on epoxy phenolics and epoxy esters are the most common.Plastic coating offers several benefits to metal objects. It acts as a barrier against moisture, preventing rust and corrosion. It also provides insulation, electrical resistance, and impact resistance, enhancing the durability and lifespan of the metal. Several research works have been published dealing with alloys and metals used in food package process and the corrosion behavior of these materials [1-10]. The main findings are summarized in Table 1.

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Table 1. Corrosion behavior of metals and alloys used in food packaging processes.

SNo/ Ref	Title	Methods employed and findings
1	Electrochemical and AFM study of inhibitory properties of thin film formed by tartrazine food additive on 304L stainless steel in saline solution	Trisodium (4E)-5-oxo-1-(4-sulfonatophenyl)-4-[(4-sulfonatophenyl) hydrazono]-3-pyrazolecarboxylate, effect on the corrosion rate of 304L stainless steel used as canned food packaging has been studied by estimating the inhibitory properties of the organic film formed on the alloy surface during the electrochemical measurements performed in saline solution containing 0.9 % NaCl, without and with tartrazine inhibitor. AFM technique revealed the main surface changes of steel corroded in saline blank solution as well as in saline solution containing tartrazine food additive compared to standard stainless steel sample.
2	An update on the innovative surgical double-glove hole puncture indication systems: Reliability and performance	During operative procedures, operating room personnel wear sterile surgical gloves designed to protect them and their patients against transmissible infections. The Food and Drug Administration (FDA) has set compliance policy guides for manufacturers of gloves. The FDA allows surgeons' gloves whose leakage defect rates do not exceed 1.5 acceptable quality level (AQL) to be used in operating rooms. The implications of this policy are potentially enormous to operating room personnel and patients. This unacceptable risk to the personnel and patient could be significantly reduced by the use of sterile double surgical gloves.
3	Testing the corrosion resistance of stainless steels during the fermentation of probiotic drink	Over recent years, food producers have devoted much attention to the production of safe foods. Simultaneously, using advanced process technologies, it has been necessary to carefully select materials for use in process equipment. Milk and its products are exposed to metal surfaces from the time they are processed, through the various stages of handling and manufacture, to the packaging of the finished products for market. The selection of suitable materials for daily use in the dairy industry cannot be governed solely by their price and mechanical properties but must also take into consideration their influence on the quality of milk products. The results indicated that Nb played the most protective role against corrosion during kefir fermentation, since the steel containing Nb but no Mo showed the lowest corrosion rate.
4	The 04Kh19AFT nickel-free stainless sheet steel	Ferrite steel 04Kh119AFT has been developed. It may be obtained by integrated alloying chrome steel by Ti and V at the controlled content of interstitial impurities. Control one the Ti and V carbonitrides precipitates of most suitable sizes enhances the ductility and deformability and makes the stamping of products of any size an forms easier. Field tests show that this corrosion-resistant steel is well welded, stamped, polished and liable to deep drawing when producing welded constructions. It is attraction for food engineering industry, automobile industry, household appliances, etc.
5	Internal corrosion in domestic drinking-water installations	Domestic drinking-water installations involve the use of a variety of plumbing materials. This paper describes the correlation between material quality, plumbing and operational conditions and water quality. Specific attention is paid to galvanized steel, copper and lead but the new plumbing materials stainless steel and plastic are also mentioned.
6	Superhydrophobic systems in food science and technology: Concepts, trends, challenges, and technological innovations	The natural phenomenon of superhydrophobicity that occurs in plants and animals has been a current topic for research and development with the goal of widening its applications. However, a more complete understanding of such surfaces is necessary to assess the effects of morphology, chemical structure, and surface roughness. In the food sector, such investigations tend to be at an early stage, although superhydrophobic surfaces (SHS) are known to hold promise for food packaging, processing, safety, and preservation. A review of the phenomenon of superhydrophobicity, the parameters to be evaluated for producing superhydrophobic surfaces, and the main impact factors is presented.

7	Effective electrodeposition of poly(3,4-ethylenedioxy-thiophene)-based organic coating on metallic food packaging for active corrosion protection	Modern technologies continuously need special materials with specific properties to adopt the desired application. Recently, numerous researches have been dedicated to the development of new food packaging materials that can ensure optimum protection of the packaged product. In this context, conducting polymers-based coatings were considered promising materials to be used as contact compounds in the packaging industries. Poly(3, 4-ethylenedioxythiophene) (PEDOT) films were electrochemically synthesized on two different metallic food packaging substrates, namely, tinplate and aluminum.
8	Passivation and Chemical Conversion Combined Multi-Elements Coating on Low Sn-Coated Steel for Corrosion Protection	In this work, the tinplate with 0.5 $g \cdot m^{-2}$ tin coating mass was prepared in order to improve the economic benefit for food packaging field. We studied this low Sn-coated steel surface state and developed a process combined Mo-Mn-Al-P coating based on its special structure.
9	Corrosion of aluminum for beverage packaging in acidic media containing chlorides and copper ions	Corrosion of aluminum packaging plays an important role concerning economic and health issues. The effect of aggressive ions on the behavior of the AA3104-H19 alloy provides knowledge to the food and packaging industries to improve materials and also minimizes losses associated with the corrosion. This study evaluated the interaction of the AA3104-H19 alloy and beverage using model solutions containing chloride and copper at levels close to those found in soft drinks. Information about the corrosion electrochemical behavior of aluminum alloys used for food and beverage is very scarce.
10	Corrosion protection of metallic archaeological artefacts using parylene based removable barrier coating	Barrier films are used in wide range of industrial fields such as microelectronics, food packaging or anticorrosion layers to protect material against external environmental influences. Using of barrier films may be an alternative way of anticorrosion protection and conservation of metallic archaeological objects and it is the aim of this study. Based on our previous work, polymer parylene (poly-p-xylylene) was chosen for preparation of thin films for this purpose thanks to its desirable properties such as excellent barrier properties, transparency and formation of conformai coating without defects.

A case study has been undertaken in this area.

CASE STUDY

EXPERIMENTAL

Ever silver Composition

Ever silver is an alloy of silver that consists of 92.5% pure silver and 7.5% other metal, usually copper [Figure 1]. The other metals in the alloy increase hardness, so the material will be durable.

Figure 1. Ever silver vessel containing curd rice

Curd

Curd is made by bacterial fermentation of milk. In this process, lactose in milk is converted into lactic acid by several probiotic microorganisms. The species involved in the fermentation depends on the temperature and humidity of the environment and may include Lactococcus lactis, Streptococcus diacetylactis, Streptococcus cremoris, Lactobacillus delbrueckii subsp. bulgaricus and Streptococcus thermophilus [11].

Boiled rice

Plain boiled rice is cooked using rice and water. Rice and water are the raw materials required to make boiled rice hence are called ingredients [12].

Preparation of Curd Rice Recipe

Curd rice is also known as thayirsaddam, dahi chawal and daddojanam. A very simple dish made using the most basic ingredients, curd and rice with an authentic south-indian tempering does not take more than 15 minutes to cook.

Easy to make, the curd rice is made by mixing rice with tempering it with mustard an green chillies. Allow the rice to cool slightly before adding the curd, to avoid the curds from splitting. Many people consider South Indian curd rice to be the best dish to carry along to school, work or travel.

We have taken the following combinations for investigation.

- Water system, (Water + Curd system), (Water +Curd + Rice system) and (Water + Curd + Rice + Salt system).

Surface characterization study

The ever silver specimens were immersed in various test solutions for a period of one day. After one day the specimens were taken out and dried. The nature of the film formed on the metal surface was analyzed by surface characterization studies such as SEM,contact angle and Vickers hardness.

Scanning electron microscopy (SEM)

The mild steel specimens immersed in various test solutions for one day were taken out, dried and subjected to the surface examination. The surface morphology measurements of the mild steel surface were carried out by scanning electron microscopy (SEM) using CAREL ZEISS make model EVO-18.

Contact angle

The contact angle measurements on the surface were performed on a VCA Optima instrument equipped with a CCD camera for imaging. The deionized water under static conditions with a drop volume of 5 µl was employed to determine the contact angle. VCA Optima XC software provided with instruments was used for fitting the drop shapes to find the contact angle of water on the surface. This measurement was repeated three times for each sample, the average values with standard deviations ±2 are reported.

Vickers hardness

The ever silver specimens immersed in various test solutions for one day were taken out, rinsed with double distilled water, dried and subjected to Vicker hardness. The Vicker hardness measurements of the mild steel surface were carried out by Shimadzu make model HMV-2T.

AC impedance spectra

AC impedance spectral studies were carried outon a CHI – Electrochemical workstation with impedance. The corrosion resistance of ever silver electrode immersed in various test solutions has been measured. A three – electrode cell assembly was used. The working electrode was Ever silver electrode. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode.

The real part (Z') and imaginary part (-Z'') of the cell impedance were measured in Ohms at various frequencies. Values of the charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated from Nyquist plots and Bode plots.

Results and discussion

Ever silver is popularly used for cookware, kitchen utensils and cutlery. This is because it is hardwearing, corrosion resistant and it doesn't affect the flavour of the food when used for food storage or production. Due to the resistance levels, foods with high acidity won't cause damage. Usually, students take much variety rice in stainless steel. In this project we have taken water, water+curd, water+curd+rice and water+curd+rice+salt (sodium chloride) systems, in a stainless steel. To identify whether ever silver has undergone corrosion or not, we have undertaken AC impedance spectra.

Analysis of results of AC impedance Spectra [Electrochemical Impedance Spectra (EIS)]

AC impedance spectra have been used to detect the formation of the film on the metal surface [13-17].

If a protective film is formed, the charge transfer resistance (R_t) increases, impedance value increases, phase angle value increases and double layer capacitance (C_{dl}) value decreases (Figure 2).

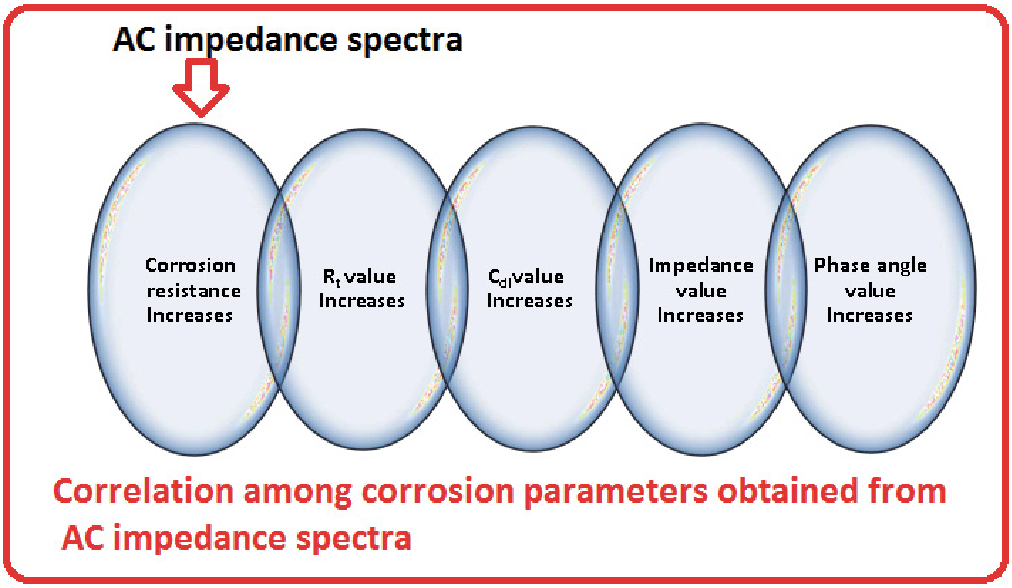

Figure 2. Correlation among corrosion parameters obtained from AC impedance spectra

The AC Impedance spectra of ever silver electrode immersed in various solutions are shown in Figures 3 to 6 (Nyquist plots) and Figures7 to 10 (Bode plots).The interactive 3D plots are shown in Figures 11 to 14.

The AC Impedance parameters, namely, charge transfer resistance (R_t), impedance value, phase angle value and double layer capacitance (C_{dl}) are given in Table 1.

Table 1. Corrosion parameters of Ever silver electrode immersed in various test solutions, obtained from AC Impedance spectra

System	Rt Ohm.cm^2	Cdl F/cm^2	Impedance Log(Z/Ohm)	Phase Angle^o
water	24.63	482.94x10^{-4}	1.675	0.0033
water+Curd	25.56	501.176x10^{-4}	2.047	0.100
Water+Curd+Rice	504	9882.35x10^{-4}	3.217	5.678
Water+Curd+Rice+Salt	32.99	646.86x10^{-4}	1.934	1.240

Let us recollect the principles of AC impedance spectra and corrosion inhibition study.

“If a protective film is formed, the charges transfer resistance (R_t) increases, impedance value increases, phase angle value increases and double layer capacitance (C_{dl}) value decreases” (Figure 2).

Interesting conclusions are derived from Table1.

Water system

When Ever silver electrode is immersed in water the charge transfer resistance (Rt) is 24.63 Ohm.cm^2. Double layer capacitance (Cdl) value is 482.94 x10^{-4} F/cm^2.

Water+curd system

When ever silver electrode is immersed in water+curd system, the corrosion resistance of ever silver electrode increases. This is due to the adsorption of molecules of the ingredients present in curd. When ever silver is electrode immersed in water+curd system the charge transfer resistance (R_t) is 25.56 Ohm.cm^2. Double layer capacitance (C_{dl}) value is 501.176x10^{-4} F/cm^2.

Water +curd+rice system

When ever silver electrode is immersed in water+curd+rice system, the corrosion resistance of Ever silver electrode further increases. This is due to the adsorption of molecules of the ingredients present in curd and boiled rice. When ever silver electrode is immersed in water+curd+rice system the charge transfer resistance (R_t) is 504 Ohm.cm^2. Double layer capacitance (C_{dl}) value is 9882.35x10^{-4} F/cm^2.

Water+curd+rice+salt system

When Ever silver electrode is immersed in water+curd+rice+salt system, the corrosion resistance of ever silver electrode decreases.

When ever silver electrode is immersed in water+curd+rice+salt system the charge transfer resistance (R_t) is 32.99 Ohm.cm^2. Double layer capacitance (C_{dl}) value is 646.86x10^{-4} F/cm^2.

When ever silver electrode is immersed in water + curd rice system + 500 ppm sodium chloride system, the corrosion resistance of ever silver electrode decreases. This is due to the presence of chloride ion introduced into the curd rice system. It implies that when curd rice is packed in vessels made of ever silver, we should avoid adding salt to the curd rice. It is better to keep the salt and curd rice separately. It is to be noted that this corrosion resistance is better than the corrosion resistance in water alone.

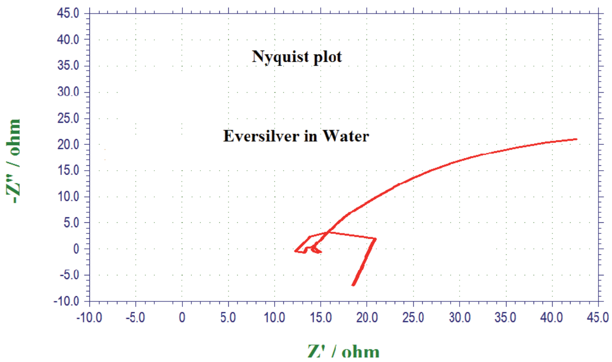

Figure 3. Nyquist plot of Ever silver electrode immersed in Water

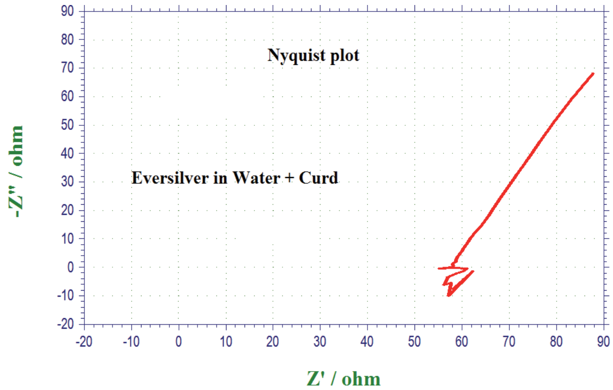

Figure 4. Nyquist plot of Ever silver electrode immersed in Water+ Curd system

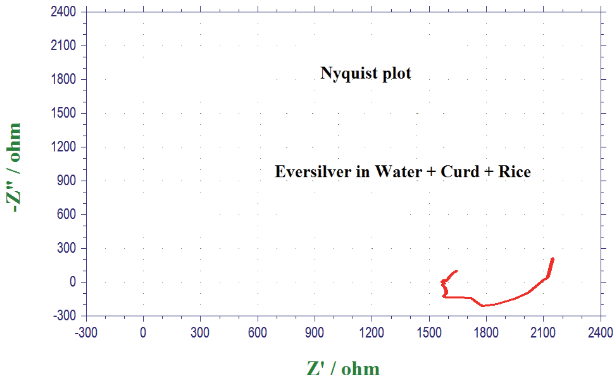

Figure 5. Nyquist plot of Ever silver electrode immersed in Water+Curd + Rice system

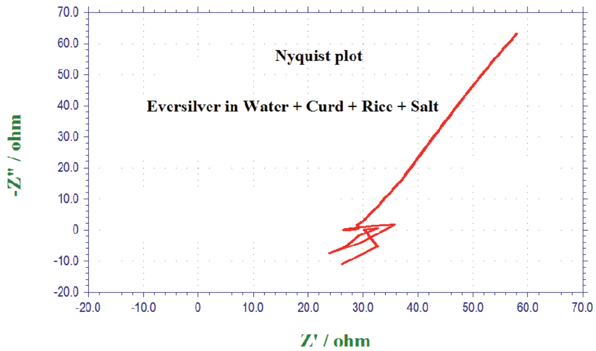

Figure 6. Nyquist plot of Ever silver electrode immersed in Water+ Curd+ Rice+ Salt system

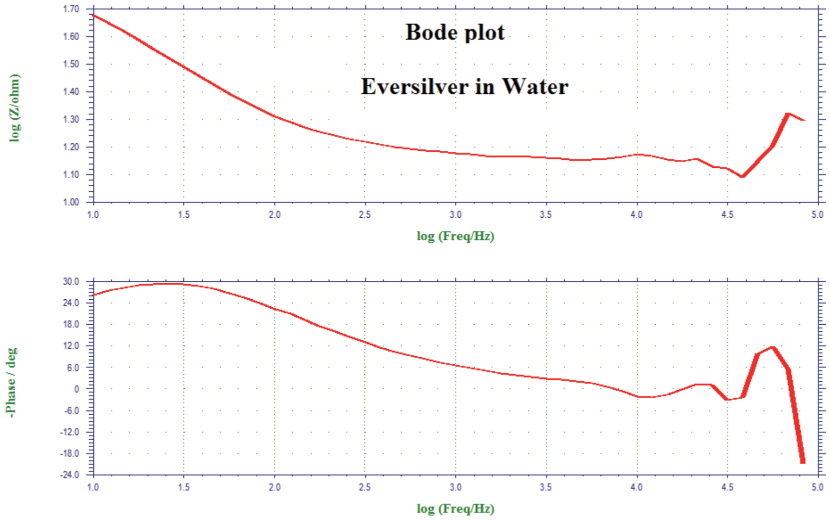

Figure 7. Bode plot of Ever silver electrode immersed inWater

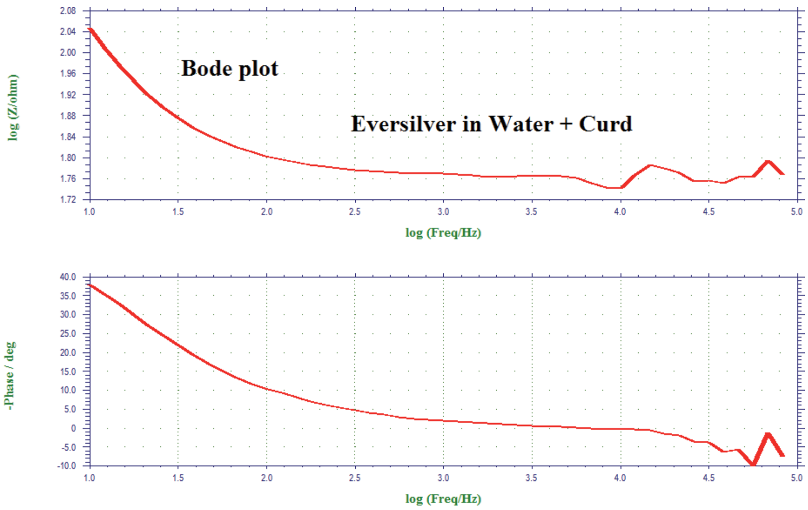

Figure 8. Bode plot of Ever silver electrode immersed in Water+ Curd system

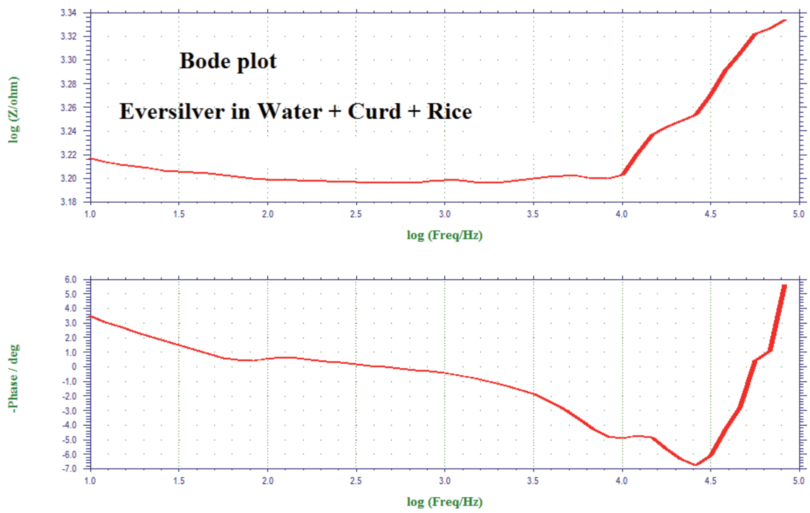

Figure 9. Bode plot of Ever silver electrode immersed in Water+Curd+ Rice system

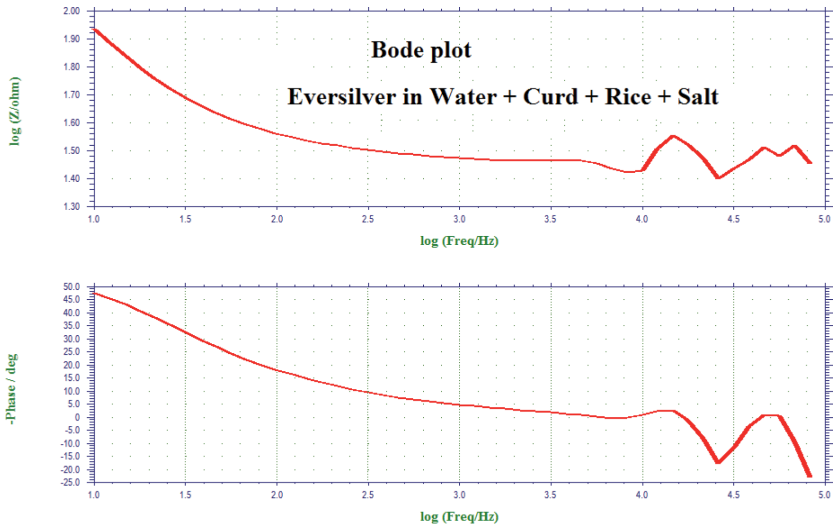

Figure 10. Bode plot of Ever silver electrode immersed in Water+Curd+Rice+Salt system

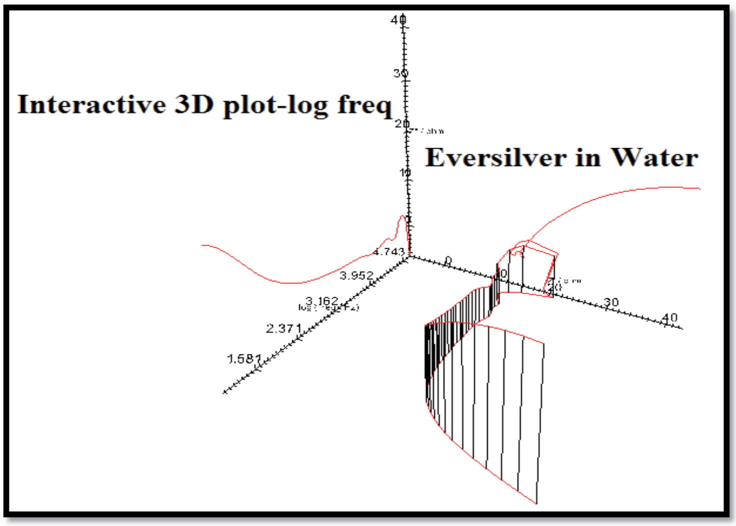

Figure11. Interactive 3D plot-log freq of Ever silver electrode immersed in Water system

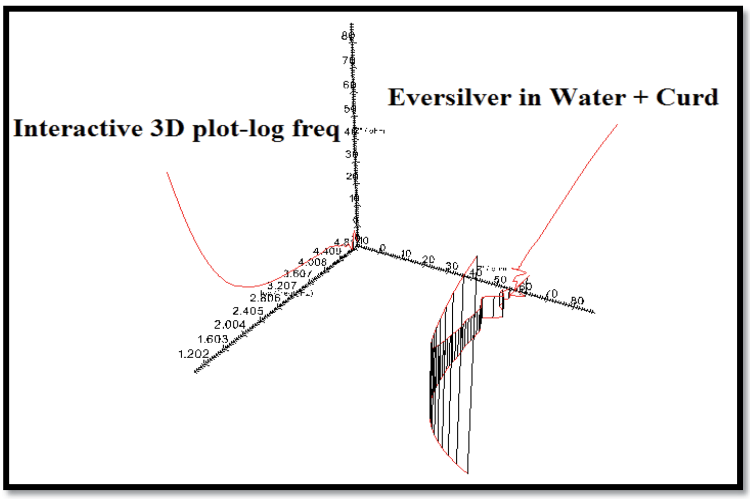

Figure 12. Interactive 3D plot-log freq of Ever silver electrode immersed inWater+Curd system

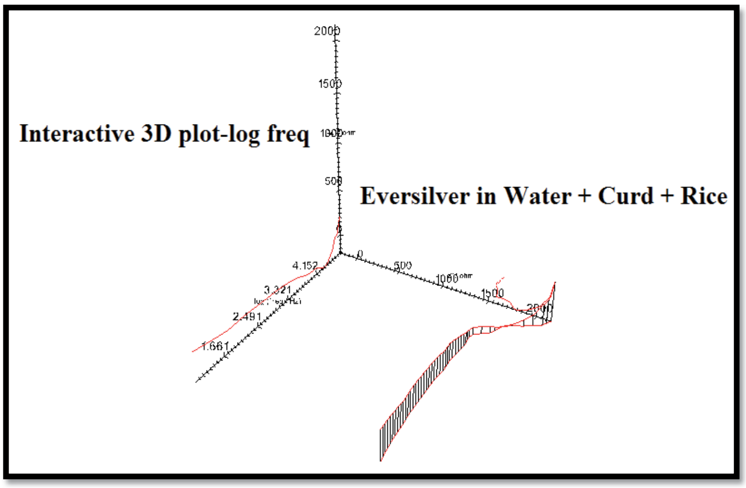

Figure 13.Interactive 3D plot-log freq of Ever silver electrode immersed in Water + Curd + Rice system

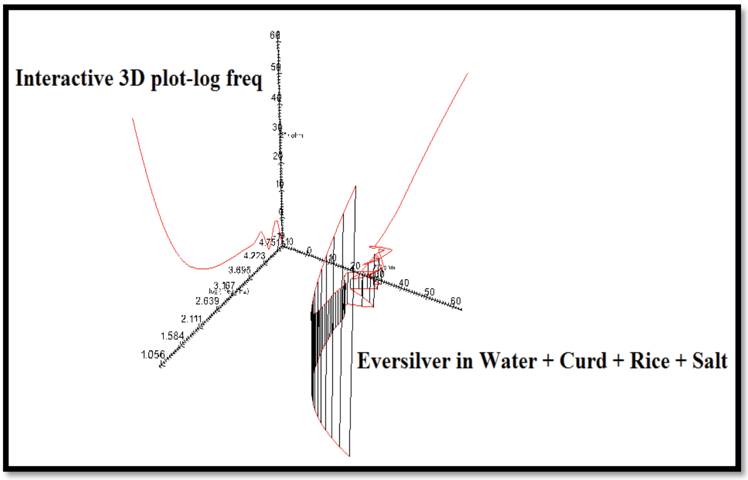

Figure 14. Interactive 3D plot-log freq of Eversilver electrode immersed in Water + Curd + Rice + Salt system

Analysis of surface morphology

Polarization study revealed that for ever silver + water + curd rice system the Charge transfer resistance value was higher (504 Ohmcm^2) than that for the ever silver + water + curd rice + salt (sodium chloride 500 ppm) system (32.99 Ohmcm^2). For these two systems surface morphology was analysed using Vickers hardness measurement, SEM and contact angle measurement.

Vickers hardness (HV)

Vickers hardness (HV) has been used to measure hardness of metal surfaces before corrosion and after corrosion process [18-22].

In the present study the Vickers hardness (HV) of ever silver in Water+Curd+Rice systemand Water+Curd+Rice+Salt system have been calculated. This is due to the following reasons. In the first system ever silver has a LPR value of 504 Ohmcm^2. But in the second system the LPR value decreases due to corrosion process induced by chloride ions introduced into the first system (Table2, Figure 15).

Table 2. Vickers hardness of various surfaces

System	Load	L1	L2	HV
Water+Curd+Rice	50 g	35.14	36.02	73.2
Water+Curd+Rice+Salt	50 g	49.41	51.79	36.2

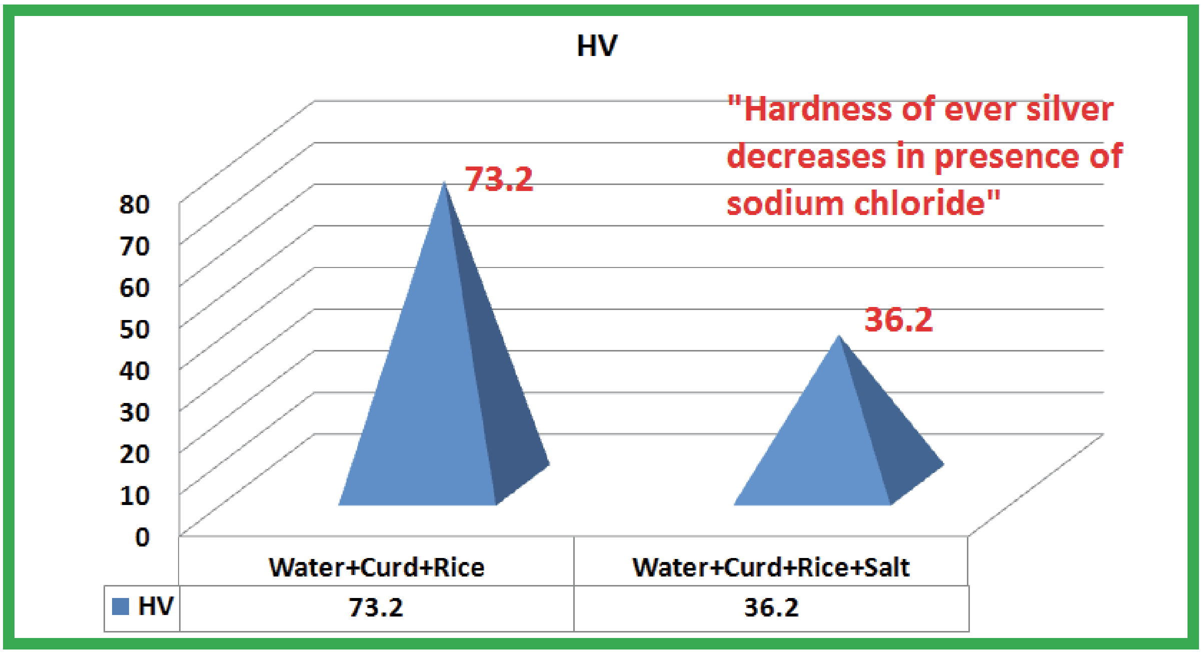

Figure 15. Comparison of Vickers Hardness values

Contact angle measurement

Contact angle measurements have been widely used in corrosion study[23-27]. The contact angles have been measured for ever silver immersed in Water+Curd+Rice systemand Water+Curd+Rice+Salt system (Figure 16). This is due to the following reasons. In the first system ever silver has a R_t (charge transfer resistance) value of 504Ohmcm^2. But in the second system the R_t (charge transfer resistance) value decreases due to corrosion process induced by chloride ions introduced into the first system. It is observed that contact angle for first system is higher (112.3°) than that for second system (99.1°). This indicates that the first system is hydrophobic (contact angle > 90°) and the later is less hydrophobic in nature. So in the first case water molecules could not reach the metal surface and so higher R_t (charge transfer resistance) value in AC impedance spectral study.

Figure16. Comparison of contact angle values

ANALYSIS OF SEM IMAGES

SEM images have been used in corrosion inhibition studies [28-32]. When the metal surface is in a corrosive medium corrosion resistance decreases and pits are noticed. The surface becomes rough. On the other hand in a corrosion protected system the metal surface is smooth. The SEM images of the surface of ever silver immersed in water + curd rice system and water + curd rice + sodium chloride (salt 500 ppm) are shown in Figure17 . It is evident that ever silver has undergone corrosion when it is immersed in water + curd rice + sodium chloride (salt 500 ppm) system. Pits are noticed on the metal surface (Figure 17).

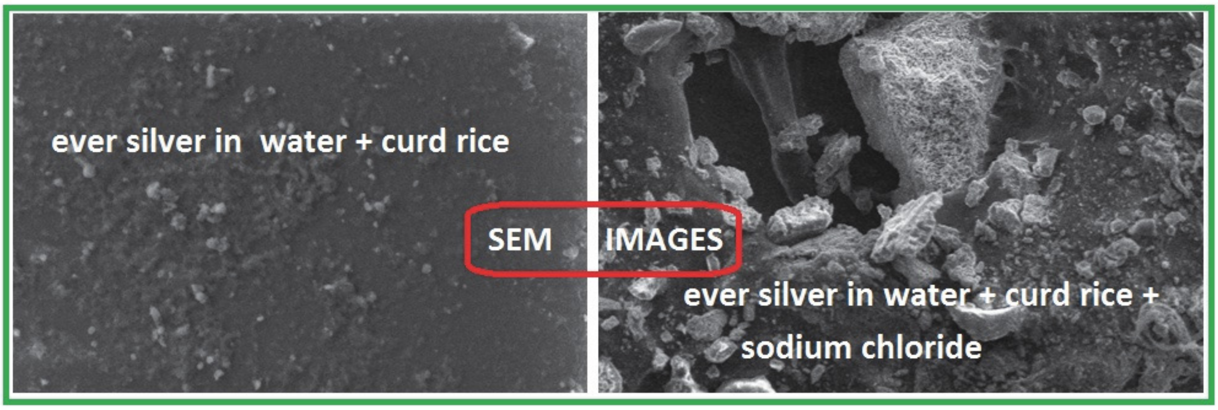

Figure 17. SEM images

CONCLUSION

- This project is undertaken to know ifEversilver vessels undergo corrosion or not, when they come in contact with some food items (recipes) .
- AC impedance spectra have been employed to investigate the corrosion resistance of ever silver electrode when it is immersed in various test solutions like water, curd, curd rice recipe, curd rice recipe with salt (sodium chloride 500 ppm).
- The corrosion resistance of eversilver electrode when it is immersed in various test solutions like water, water+curd, water+curd+rice and water+curd+rice+salt have been evaluated by AC impedance spectroscopy.
- If a protective film is formed, the charge transfer resistance increases, impedance value increases, phase angle value increases and double layer capacitance (C_{dl}) value decreases.
- When Ever silver electrode is immersed in water + curd rice system + 500ppmsodium chloride system, the corrosion resistance of eversilver electrode decreases. This is due to the presence of chloride ion introduced into the curd rice system. It implies that when curd rice is packed in vessels made of eversilver, we should avoid adding salt to the curd rice. It is better to keep the salt and curd rice separately. It is to be noted that this corrosion resistance is better than the corrosion resistance in water alone.
- The corrosion resistance decreases in the following order:

Water + Curd + Rice system > Water + Curd + Rice + Salt system (sodium chloride 500ppm) >Water+Curd system > Water

SCOPE FOR FURTHER STUDIES

The present work is undertaken to investigate the corrosion inhibition of ever silver in the presence of water, water+curd system, water+curd+rice system, water+curd+rice+salt system. The corrosion resistance has been evaluated by AC impedance spectra .

In future the following study can be undertaken

- Instead of curd other food item can be used.
- Instead of ever silver other metals can be used.
- Surface analysis such as AFM, FTIR, EDAX., can be employed.

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IZVOD

UTICAJ NATRIJUM HLORIDA NA OTPORNOST NA KOROZIJU SREBRNIH POSUDA U PRISUSTVU PIRINČA

Ovaj rad je napisan kako bi se istražila otpornost na koroziju srebra u prisustvu vode, sistema voda+gruša, sistema voda+skuta+pirinač, voda+sir+pirinač+so. Otpornost na koroziju je procenjena spektrima impedanse naizmenične struje. Spektri impedanse naizmenične struje su korišćeni da se ispita otpornost na koroziju srebrne elektrode kada je uronjena u različite test rastvore kao što su voda, skuta, recept za sirni pirinač, recept za sirni pirinač sa solju (natrijum hlorid 500 ppm). Otpornost na koroziju srebrene elektrode kada je uronjena u različite test rastvore kao što su voda, voda+sir, voda+skuta+pirinač i voda+suta+pirinač+sol procenjena je spektroskopijom AC impedanse. Ako se formira zaštitni film, otpor prenosa naelektrisanja se povećava, povećava se vrednost impedanse, povećava se vrednost faznog ugla i smanjuje se vrednost kapacitivnosti dvostrukog sloja (Cdl). Kada se srebrna elektroda uroni u vodu + sistem pirinča + 500ppms sistem natrijum hlorida, otpornost na koroziju svake srebrne elektrode se smanjuje. Ovo je zbog prisustva hloridnog jona unešenog u sistem skute pirinča. To implicira da kada se pirinač pakuje u posude napravljene od srebra, treba izbegavati dodavanje soli u skutu. Bolje je držati so i skutu odvojeno. Treba napomenuti da je ova otpornost na koroziju bolja od otpornosti na koroziju samo u vodi.

Otpornost na koroziju se smanjuje sledećim redosledom:

sistem voda + skuta + pirinač > voda + skuta + pirinač + so sistem (natrijum hlorid 500ppm) > sistem voda + skuta > voda

***Ključne reči:** otpornost na koroziju, srebro, skuta, natrijum hlorid, elektrohemijska ispitivanja*

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