Ferrocene Complexes With Heteropolyacids For Corrosion Inhibition Studies

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Abstract:

Corrosion is a global problem for any metallic structure or material. One major approach to prevent corrosionistheuseofcorrosion-protectivecoatings.Inthepresentstudy,wehavesynthesizedhybridmolecular materials containing ferrocene and Keggin units, which have been explored for corrosion inhibition of stainless steel (316 grade) in acidicmedium.

The design of organic-inorganic hybrid materials is a potential pathway for the development of novel materialswithuniqueredoxand catalyticproperties.Bothferroceneand heteropolyacidshavebeenindividually wellstudiedinthefieldsofcatalysisandelectrochemistry[1-3].Thesynthesesofthehybridmolecularmaterials were carried out in acidic medium, as the Keggin ions are stable in low pH. Also, the ferricinium ion generated in acidic medium readily co-precipitates with phosphotungstic acid and phosphomolybdic acid. The molecular formula of the resulting hybrid materials (FcPW and FcPMo) is $[Fe(y^5\text{-}Cp)_2]_3P(W_{12}/Mo_{12})O_{40}$. The hybrid materials were characterized using UV-Vis DRS, FTIR, powder XRD and FESEM images. Further, these materials have shown corrosion inhibition properties on stainless steel (316 grade) plates in acidic solution as inferred from weight loss method, impedance spectraand Tafelplots.

Keywords: Corrosion, SS 316, Ferrocene, Heteropolyacids, Keggin

1. Introduction

Polyoxometalates (POMs) are a group of polyatomic compounds containing multiple transition metal ions (like Mo,W) linked together in a 3D frame work by shared oxygen atoms.Unlike many metaloxide sand polyoxoion salts,polyoxometalates comprising early transition elements are readily soluble in water. The polyoxometalates can be classified into isopolyoxometalates; heteropolyoxometalates; mixed-addend apolyoxometalates; lacunary polyoxometalates and transition-metal substituted polyoxometalates [4]. The general formula is$[M_mO_y]^{p-}$for isopolyanions and $[X_xM_mO_y]^{q-}$(for $x<=m$) for heteropolyanions (i.e. having a metal, heteroatom and oxides). The structures of polyoxometalates isolated are Lindquist, Keggin, Wells-Dawson, Anderson-Evans, Preyssler,etc. [5]. The metal, M, generally is a metal ion having favorable ionic radius and charge. Hence, it is capable of forming *d*n-*p*nM–O bonds. M can be molybdenum, tungsten, and in few cases, vanadium, niobium or tantalum in their highest oxidation states[6].

Ferrocene $[Fe(y^5\text{-}Cp)_2]$ is an iron containing metallocene having electron donor-acceptor conjugated structure [7]. It is non-toxic, lipophilic, insoluble in water, and has efficient redox couple(Fe^{2+}/Fe^{3+}). In acidic medium, oxidation of $[Fe(y^5\text{-}Cp)_2]$ to $[Fe(y^5\text{-}Cp)_2]^+$(ferricinium cation) occurs which is characterized by deep red coloration [7].

The hybrids synthesized can have applications in photocatalysis, where they can act similar to Fenton reagent[8]. This is because on irradiation with light energy high erore qual to the HOMO–LUMO gap of POMs, electron-transfer from $O^{2"}$

to M^{6+} (M = W, Mo) occurs, forming excited POMs [9]. These excited POMScan oxidize $Fe^0$to Fe^{2+} state, forming Fenton-like reagent that can degrade organic pollutantsin the presence of hydrogen peroxide [10]. In this paper, however, the combinatorial corrosion inhibition properties of both ferrocene and polyoxometalates have been explored using stainless steel plates (316) grade in acidic medium. Hence, the seorganic-inorganic materials seemto have both catalyticand corrosion in hibition properties.

2. Experimental

In the present study, we have synthesized complexes of ferrocene with phosphomolybdic and phosphotungstic acids, which is pictorially represented in Fig. 1.

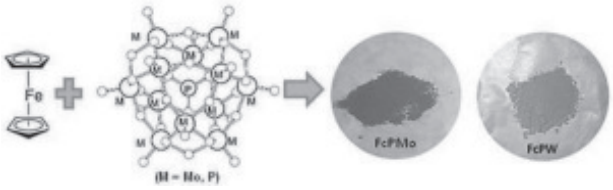


Figure 1Synthesis of hybrid materials of ferrocene and heteropolyacids (FcPW and FcPMo).

Ferricinium ion was generated in acidic medium, rendering the solution deep red in colour, which co- precipitates with phosphotungstic acid and phosphomolybdic acid to form azure precipitate. The ferricinium cation interacts with the anionic cluster of the Keggin structure to form charge transfer hybrid salt with molecular formula $[Fe(\psi^5\text{-}Cp_{23})]^+ P(W/Mo_{1240}) O$.

3. Results andDiscussion

3.1 FTIRSpectra

The FTIR spectra were recorde dusing JASCOFT/ IR4100 spectrometer in the range 400-4000cm^{-1}. The FTIR spectra of ferrocene, phosphotungstic acid, phosphomolybdic acid, FcPW and FcPMo are shown in Fig. 2. The character isticab sorptionband sofferrocen eare3095cm^{-1}, (vC-H), 1405, 1103cm^{-1}(vC=C),1000cm^{-1}(þC-H), 818 cm^{-1}(vC-H) and 475 cm^{-1}($v_{as}Fen_6$, $v_{as}n_6n_6$) [10]. The Keggin signature of PWA shows vibrations at 810 cm^{-1} ($v_{as}W–O_c–W$), 895 cm^{-1} ($v_{as}P=O$), 981 cm^{-1} ($v_{asW=O}$) [11]. The absorption bands at 1078 cm^{-1} and 1630 cm^{-1}(significantly weakened vC=C) implies the existence offerricinium cationin FcPW. The Keggin signature peaksof PMoA at 790cm^{-1} ($v_{as}Mo–O_c–Mo$), 870cm^{-1}($v_{as}P=O$), 961cm^{-1}($v_{as}Mo=O$). The absorption bandsat 1616 and 1063cm^{-1}(significantly weakened v C=C) implies the existence offer riciniumcation in FcPMo. Thus, Keggin signature peaks as well as ferrocene characteristic peaks can be seen in the hybrids, indicating that the cationic and anionic moietiesare intact.

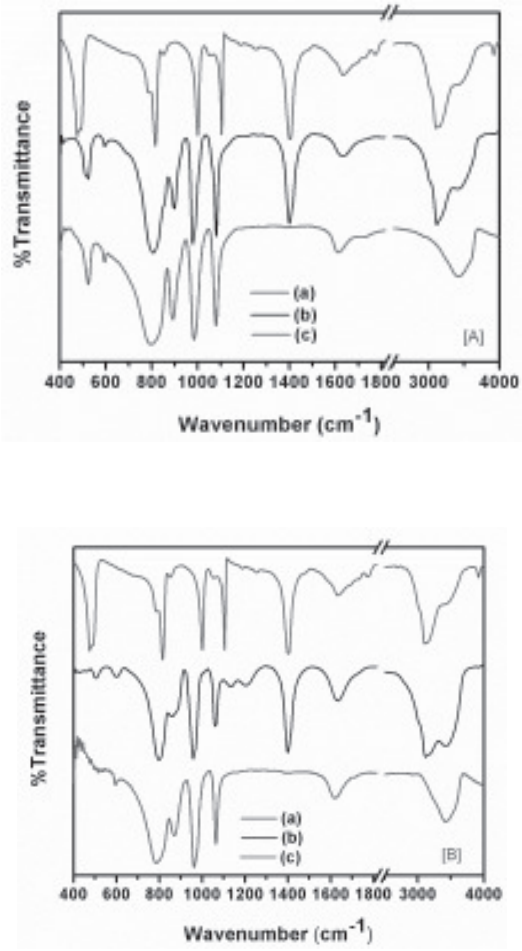


Figure 2 FTIR spectra for (A): (a) Ferrocene, (b) FcPW and (c) phosphotungstic acid; (B): (a) Ferrocene, (b) FcPMo and (c) phosphomolybdic acid.

3.2 UV-VisAnalysis

The UV-Visible spectrophotometer for the solid samples was recorded using JASCO V-660 UV-visible spectrometer. The UV–Vis DRS of ferrocene, phosphotungstic acid, phosphomolybdic acid, FcPW and FcPMo are

shown in Fig. 3. The absorption bands of ferrocene around 330 and 470 nm are assigned to ligand field bands from the splitting of the d levels of Fe^{2+} [10]. FcPW and FcPMo each display an absorption band at ca. 200–450 nm due to charge transfer from O_2 to W^{6+}/Mo^{6+} at W=O (or Mo=O) and W-O-W (or Mo-O-Mo) bonds. Further, they also show a broad absorption band peaked at ca. 620 nm due to charge transfer from ferricinium ion to polyoxometalate ion.

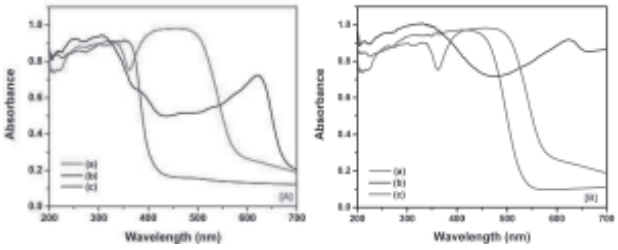


Figure 3 UV-Vis DRS for (A): (a) Ferrocene, (b) FcPW and (c) phosphotungstic acid; (B): (a) Ferrocene, (b) FcPMo and (c) phosphomolybdic acid.

3.3 Powder XRDanalysis

The samples were analyzed by Powder X-Ray Diffraction using BRUKER AXS D8 advanced diffractometer at room temperature with Cu Ká radiation (Z= 1.54 Å). The peaks obtained in the hybrid for low angle measurements indicate layered structure (Fig. 4) [11]. For FcPW, the 20values obtained are 7.8°, 8.7° and 9.3° which correspond to(111), (200) and (020); while for FcPMo, the 20 values obtainedare 8.5°, 8.9° and 9.7° which correspond to (111), (200) and (020).

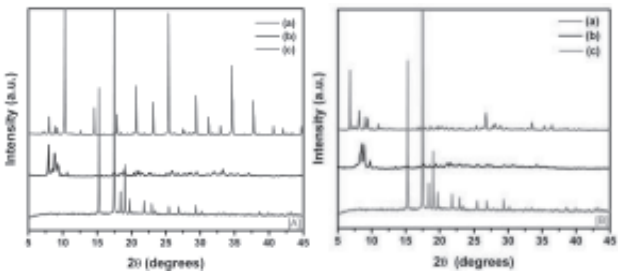


Figure 4 PXRD plot for (A): (a) phosphotungstic acid, (b) FcPW and (c)ferrocene; (B): (a) phosphomolybdic acid, (b) FcPMo and (c)ferrocene.

3.4 FESEMAnalysis

SEM images were taken using a FEI Quanta 450 microscope operating at 30 kV in low vacuum. The sample powders were deposited on a carbon tape before mounting on a sample holder. The SEM analyses showthat the hybrid materials formed show powdery morphology with small clusters adhered together (Fig. 5) [12].

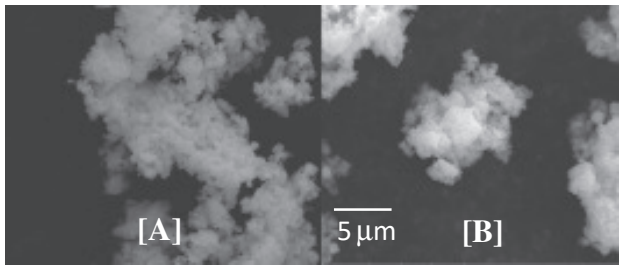


Figure 5 SEM images of hybrid salt of (A) FcPW and (B) FcPMo.

3.5 Application

For corrosion inhibition studies, weight losses, electronic impedance spectroscopy and Tafel plots were recordedand the results are shown in Table 1. Working electrode: Stainless steel (316 grade) with FcPMo/FcPW; Counter electrode: Pt wire; Reference electrode: Ag/AgCl; Electrolyte: 0.5 M H_2SO_4.

The composition of 316 gradeste elisFe(1%), C(0.03%), Cr(16-18.5%); Ni(10-14%); Mo(23%); Mn(2%); Si(1%); P(0.045%); S(0.03%)[13]; molecularweight =20.376g/mol;density=7.87g/cm^3; areaofelectrode=5x1 = 5 cm^2; exposed area = 1 cm^2. The reactions taking place during corrosionare:

Anodic reaction: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
Cathodicreaction:$2H^+(aq)+2e^- \rightarrow H_2(g)$

Weight loss method: The rectangular specimens of 316 grade SS with area 5 ´ 1 $cm^2$and exposed area 1 cm^2 were mechanical lyabraded with sandpaper of grit size 3000, and emery paper of 5/0 grade. The weight loss was measured by immersing (a) blank stainless steel plate, (b) stainless steel plate coated with FcPMo and (c) stainless plate coated with FcPW, in 0.5 M H_2SO_4for24 hrs. Then the steel plates were taken out, washed with distilled water, dried and

weighted again to determine the weight loss, corrosion rate and corrosion inhibition efficiency (measured in millimeter per year, mmy)[14,15].

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Electronic impedance spectroscopy: Impedance spectra of the blank steel electrode and that of steel electrode coated with FcPW and FcPMo are recorded. Comparing the Nyquist plots as shown in Fig. 6[A], the charge transfer resistancesare found as SS = 927.64 ohm, SS coated with FcPW = 6480.52 ohm, SScoated with FcPMo

= 7363.7 ohm. From these values the corrosion inhibition efficiency was calculated

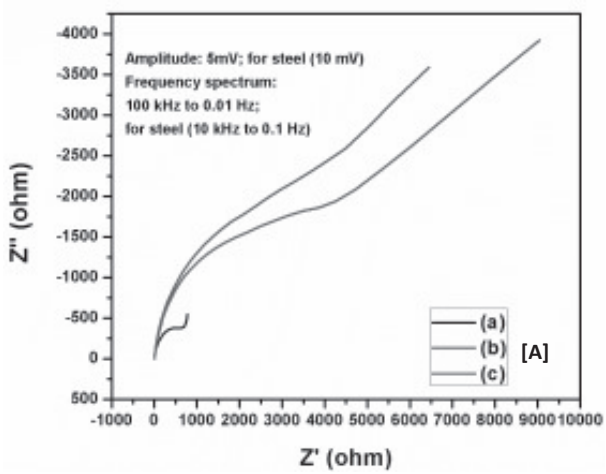
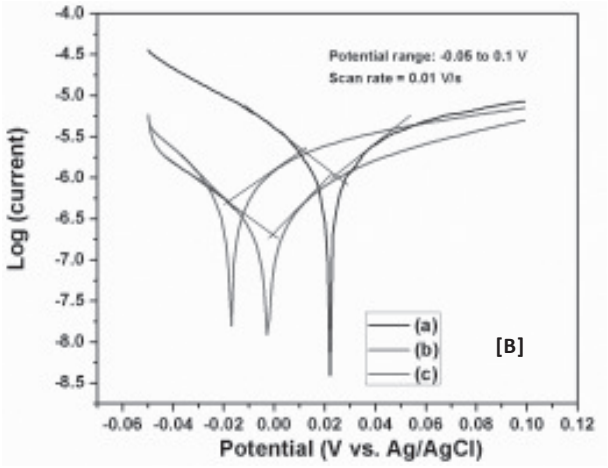


Table 1 Corrosion rate and inhibition efficiency of the blank stainless steel electrode, and the electrodes coated with hybrid materials.

Electochemical Impedance Spectroscopy	**Tafel Plots**	**Weight Loss Measurements**
EIS of the electrodes were recorded and Nyquistplots obtained.	Tafel plots of blank steel and coated electrodes were recorded.	Weight loss measured byimmersing the electrodes in 0.5 M H_2SO_4for24 hours.
	$\text{Rate} = \frac{\text{icorr} \times \text{M}}{\text{n} \times \text{F} \times \text{d}}$	$\text{Rate} = \frac{\text{Wt. loss} \times 8.75 \times 10000}{\text{d} \times \text{A} \times \text{t}}$
$\psi\% = \frac{\text{Rct} - \text{Rct, steel}}{\text{Rct}} \times 100$	$\psi\% = \frac{\text{icorr,steel} - \text{icorr}}{\text{icorr,steel}} \times 100$	$\psi\% = \frac{\text{Rcorr,steel} - \text{Rcorr}}{\text{Rcorr,steel}} \times 100$
Corrosion inhibition efficiency: 1. SS coated with FcPMo =87.4% 2. SS coated with FcPW =85.6%	**Corrosion rate:** 1. Blank SS =2.138mmy 2. SS coated with FcPMo = 0.667mmy 3. SS coated with FcPW = 0.876mmy **Corrosion inhibition efficiency:** 1. SS coated with FcPMo =84.4% 2. SS coated with FcPW =60.8%	**Corrosion rate:** 1. Blank SS =15.15mmy 2. SS coated with FcPMo =0.092mmy 3. SS coated with FcPW = 0.14mmy **Corrosion inhibition efficiency:** 1. SS coated with FcPMo =99.3% 2. SS coated with FcPW =99.1%



Tafel plots: The Tafel plots of the blank steel electrode and that of steel electrode coated with FcPW and FcPMowere recorded and presented in Fig. 6[B].Calculations from Tafel Plots provided $E_{corr}$and i_{corr} values for SS and SS coated electrodes which were used to obtain the percentage corrosion inhibition and corrosion rate.

4. Conclusions

Ferrocene based hybrid materials were synthesize dusingphosp hot ungsticand phosphomolybdi cacidsin which ferrocene acts as an electron donor and polyoxometalate ion as electron acceptor. The charge transfer from ferrocene to poly oxometalateion was clearly was observedasa very broad absorptionb and peaked at 620 nmin UV-Vis diffuse reflectance spectra of the hybrid material. Further, peaks characteristic of ferricinium and Kegginion sinthemolecular hybridmaterials were observed from the character is tic FTIR spectral features. Both powder XRD and SEM images showlay eredstructure of the hybrids. The hybridmolecular materials were found to possesssignificant corrosion inhibition properties on stainless steel (316 grade) plates in 0.5 MH_2SO_4as depicted fromweight loss method, impedance spectraand Tafelplots.

5. References

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