

Synopsis of the thesis entitled

**CATALYTIC AND ELECTROCHEMICAL EXPLOITATION
OF POLYOXOMETALATES**

to be submitted by

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for the award of the degree

of

DOCTOR OF PHILOSOPHY

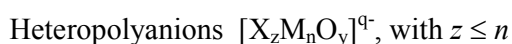
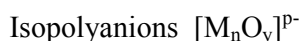


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1. INTRODUCTION

Polyoxometalates (POMs) are metal oxide clusters, discrete and well defined at atomic level with extensive structures and properties. They constitute an extremely large and diverse class of compounds (Pope, 1983; Pope and Muller, 1991). POMs are generally characterized by a metallic ion center, M, which is surrounded by oxygen atoms (MO_n units). Apart from M and O, other elements such as X, can be a part of the POM framework. Depending on whether X is present or not, POMs can be classified into two types.



Where X is called as heteroatom and M is called as addendum atom. POMs, due to their unique physicochemical properties are widely used as homogeneous and heterogeneous acid and oxidation catalysts and found several industrial applications (Pope and Muller, 1991). In recent applications, they have been used as homogeneous and supported catalysts in electrophilic transformations (alkylation, acylation, isomerization, hydration, dehydration) of various organic molecules. They are also of great interest as model systems for studying fundamental problems of catalysis (Okuhara *et al.*, 1996). High Brønsted acidity of POMs compared to that of traditional mineral acid catalysts is of great relevance in catalysis (Kozhevnikov, 1998). Many new catalytic processes for basic and fine organic syntheses have been developed using POMs. POMs have also been found as potential catalysts in various electrochemical processes because of their interesting properties such as high stability of most of their redox states, tunability of the redox behavior by changing the heteroatoms and addenda atoms without affecting their structure. According to Katsoulis' compilation (Katsoulis, 1998) there were more than 700 communications (publications and patents) in the family of POMs. Most applications are related to their special ability to accept one or several electrons with minimal structural changes. Their remarkable chemical and physical properties have led to a variety of potential applications in medicine, catalysis, solid-state technology, and chemical analysis (Baker and Glick, 1998).

2. MOTIVATION AND SCOPE OF THE WORK

Among various types of POMs that exist, Keggin type POMs are studied extensively. The Keggin anion, of general formula $H_{8-x}[X^xM_{12}O_{40}]$ (where X is the heteroatom

(e.g. P^{5+} or Si^{4+}), x the oxidation state, and M is the addendum atom (usually Mo^{6+} or W^{6+}) has been the focus of much effort for the understanding of the chemistry of POMs. A simple synthetic route as well as the flexibility of its chemical composition makes these compounds the main reference for the knowledge of the general behavior of metal-oxide clusters and, especially, POMs. The most common and thermally stable primary structure of POMs is that of the Keggin unit. Keggin type POMs are fairly stable, constitute rich redox properties, easily available and have been studied in more detail. Investigations of catalytic properties in the solid state have been mostly devoted to this class of POMs (Misono, 1987). Exploitation of the physicochemical properties of Keggin type POMs for various applications is an essential task. Therefore, the work done in this thesis is projected at the exploitation of Keggin type POMs for potential applications in catalytic and electrochemical processes. The thesis work is focused on the following aspects:

- The high Brønsted acidity with low toxicity of POMs is characteristic of POM. This has been well exploited for fine chemical synthesis. In this direction, POMs have been utilized as catalysts for the synthesis of Polylactic acid (PLA) and chloromethyl methyl ether (MOM-Cl). Where in, high Brønsted acidity of Keggin type POMs have been successfully exploited.
- POMs rich redox properties have been utilized for various applications. In this context, electron transfer ability of POMs has been well utilized for (i) the preparation of metal nanoparticle supported on carbon-POM nanocomposites (Pt/POM-C, Pt-Ru/POM-C, Ru/POM-C and Pd/POM-C) and (ii) for the synthesis of metal nanoparticles embedded conducting polymer-POM nanocomposites wherein, sequential reactions have been performed by single reagent.
- POMs have functioned as electrocatalysts and promoters for various electrochemical processes. In this regard, the synthesized nanocomposites containing metal nanoparticles supported on carbon have been exploited for electrochemical energy conversion (Fuel cell electrocatalysts) and storage (Electrodes for electrochemical supercapacitors) applications.
- The ability of POMs association in multi-component composites can be exploited for the preparation of various materials. Metal carbides (WC and Mo_2C) have been prepared by the decomposition of polypyrrole – POM composites with out the addition of carbon.

3. SUMMARY OF THE RESEARCH WORK

3.1. Synthesis of polylactic acid (PLA) using Keggin type POM

Poly(lactic acid) (PLA) is versatile, biodegradable, aliphatic polyester derived from 100% renewable resources such as corn and sugar beets. PLA offers great promise in a wide range of commodity applications. In the present study a solid acid catalyst, tungstophosphoric acid $H_3[PW_{12}O_{40}]$ was employed as the polycondensation catalyst for the polymerization of lactic acid. The prepared PLA was well characterized by using FT-IR, 1H NMR and ^{13}C NMR. The thermal characteristics of the polymer have been studied using TGA and DSC analyses. Fig. 1 shows ^{13}C NMR of the synthesized PLA using $H_3PW_{12}O_{40}$ as the catalyst.

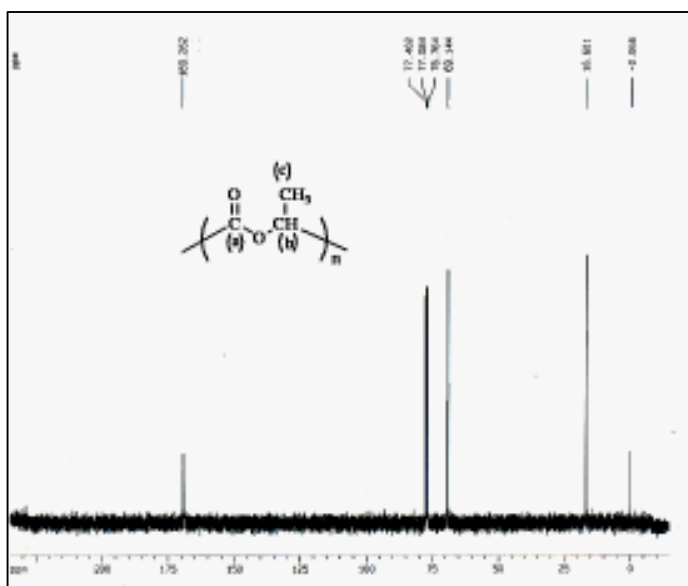


Fig. 1 ^{13}C NMR of the synthesized PLA, using $H_3PW_{12}O_{40}$ as catalyst.

The peaks appearing at 169.510, 69.144 and 16.601 ppm originated from the carbon of (a) $-COOH$, (b) $-C-OH$, and (c) $-CH_3$ groups respectively. The peaks due to the solvent ($CDCl_3$) appeared around 77 ppm. Thermal characteristics of synthesized PLA such as glass transition temperature and decomposition temperature were obtained from the TGA and DSC analyses. PLA exhibited a glass transition at 59 °C and also a decomposition temperature around 370 °C. The data relevant to the magnitude of the molecular weight were obtained by GPC analysis in terms weight average molecular weight (M_w) and number average molecular weight (M_n). Furthermore the polydispersity index which is a measure of the molecular weight distribution was obtained by GPC. The obtained PLA exhibited a molecular weight of (M_w) 42,000 K with low polydispersity index (1.07).

MOM-Cl was characterized by using ^1H & ^{13}C NMR. In Table 1, the catalytic activities of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ are compared.

Entry	Catalyst	Yield ^a (%)	TON ^b	TOF ^c (h ⁻¹)
1	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	79	104	26
2	$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	66	65	16
3	$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	59	49	12
4	$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$	58	87	21

Table. 1 Effect of various POMs in the synthesis of MOM-Cl

^a Isolated yield

^bTON : Moles of MOM-Cl produced per mole of catalyst

^cTOF : Moles of MOM-Cl produced per mole of catalyst per hour

The results of this study show that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is an effective catalyst for this purpose which is due to its highest acidity ($\text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_4\text{SiW}_{12}\text{O}_{40} \geq \text{H}_3\text{PMo}_{12}\text{O}_{40}$) compared to all other catalysts studied (Misono et al., 1982). As compared to H_2SO_4 catalyzed reaction (in this case a 64 h reaction time was required) (Reggelin and Sebastin, 2004), turn over number and frequency values (TON & TOF) are considerably high for the POM catalyzed reaction.

3.3. Exploitation of POM, silicotungstic acid (STA) for the preparation of carbon supported metal nanoparticles

For further utilization of Pt and Pt-Ru based composites as fuel cell electrocatalysts, Pt or Pt-Ru loadings in the composites were done at the nominal Pt level in the commercial catalyst, i.e., 20 wt% of Pt or Pt-Ru. The typical procedure involved the following steps. Specific amounts of hexachloroplatinic acid (10mM) or hexachloroplatinic acid (10mM) and ruthenium (III) chloride hydrate (10mM) have been loaded on carbon to get 20 wt% metal loading by conventional impregnation method. The composition of Pt and Ru was fixed to produce a final atomic ratio of 1:1 in the preparation of all Pt-Ru based composite catalysts. The mixture was magnetically stirred for 3h at room temperature and then evaporated to dryness at 80°C. Reduced STA (10mM) was added to the impregnated material, followed by microwave irradiation for 90 s. The colour of the reduced STA has changed from blue

to colourless indicating the oxidation of STA, ensured the electron transfer from STA to metal ions. Facile electron transfer drives the reduction of metal ions. The final solid products of 20% Pt/STA-C and 20% Pt-Ru/STA-C were obtained by centrifugation, washed with water and then dried in vacuum at 70 °C for 8h. Similar procedure was adopted for the preparation of Pd/STA-C and Ru/STA-C by replacing 10 mM hexachloroplatinic acid (10mM) with that of aqueous solutions of 10 mM ruthenium chloride and 10 mM palladium chloride respectively. The prepared nanocomposites were well characterized by using FT-IR, XRD, TEM, HRTEM and EDX analysis.. Fig. 2a & b show the representative TEM micrographs of the Pt/STA-C and Pt-Ru/STA-C and the corresponding particle size distribution analysis are presented in figure 3a & 3b respectively.

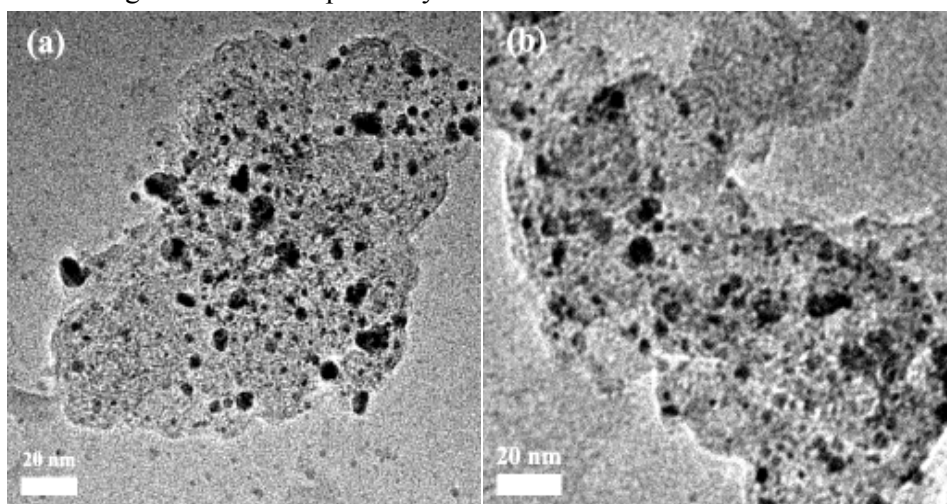


Fig. 2 TEM images of (a) Pt/STA-C and (b) Pt-Ru/STA-C

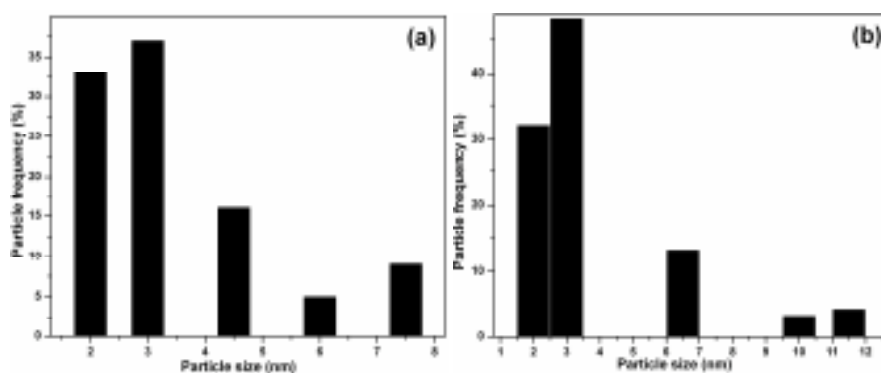


Fig. 3 Particle size distribution curves of (a) Pt/STA-C and (b) Pt-Ru/STA-C

The TEM images of Pt/STA-C & Pt-Ru/STA-C nanocomposites show highly dispersed metal nanoparticles on the carbon support. A statistical analysis of the TEM image shows that, Pt nanoparticles have an average diameter of 2.8 nm, with a size distribution standard deviation of 1.8 nm in the Pt/STA-C composite. Pt-Ru nanoparticles have an average diameter of 3.6 nm, with a size distribution standard

deviation of 2.4 nm in Pt-Ru/STA-C composite. In order to compare the efficiency of the STA reduction method, a second set of Pt and Pt-Ru nanoparticles dispersed on carbon (Pt/C and Pt-Ru/C) were prepared using H₂ reduction method. The prepared nanocomposites using STA showed relatively small particles with good dispersion over the nanocomposites produced under H₂ atmosphere at high temperature.

3.4. Synthesis of metal nanoparticle embedded conducting polymer-POM nanocomposites

The desire to synthesize nanostructures that combine the mechanical flexibility, optical and electrical properties of conducting polymers with high electrical conductivity and magnetic properties of metal nanoparticles has inspired the development of several techniques for the controlled fabrication of metal nanoparticle–conducting polymer composites. The strong oxidizing potential and acidic character of Phosphomolybdic acid (H₃PMo₁₂O₄₀ or PMo₁₂) provides perfect environment for the polymerization of monomers such as aniline, pyrrole or thiophene to yield the corresponding polymer-polyoxometalate composites. The present investigation is focused on the synthesis and characterization of Au or Ag nanoparticles embedded PANi-PMo₁₂ composites (Ag-PAni-PMo₁₂ and Au-PAni-PMo₁₂). During the oxidation of aniline, PMo₁₂ gets reduced to heteropoly blue which then served as reducing agent for the metal (Ag and Au) ions to form metal nanoparticles. Fig. 4 shows the HRTEM images of the Ag and Au nanoparticles in the prepared nanocomposites.

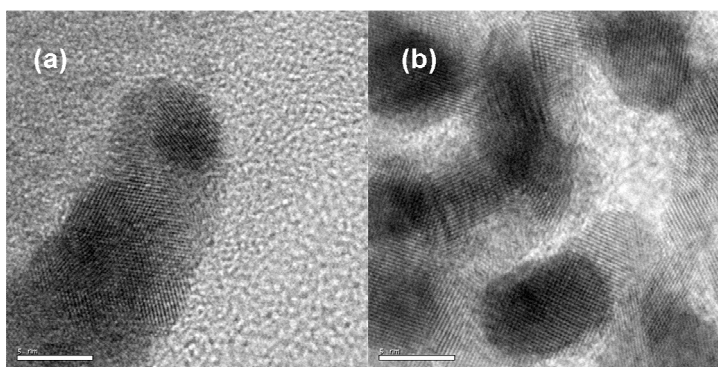


Fig. 4 HRTEM images of (a) Ag-PAni-PMo₁₂ and (b) Au-PAni-PMo₁₂

Spherical silver nanoparticles embedded in PANi polymer in the Ag-PAni-PMo₁₂ composite (Fig. 4a) have clear crystalline planes aligned along a specific direction with a d spacing of 2.36 Å. Fig. 4b indicates the dark Au nanorod arms surrounded by a grayish sheath of PANi in the Au-PAni-PMo₁₂ composite. The planes of the rods are aligned with a 'd' spacing of 2.38 Å. The synthesized nanocomposites have also been characterized by using FT-IR, XRD, BET, pore size, SEM, TEM analyses.

3.5. Exploitation of metal nanoparticles supported on carbon-POM nanocomposites for fuel cell and electrochemical supercapacitor applications

3.5.1. Pt/STA-C and Pt-Ru/STA-C as anode electrocatalysts for direct methanol fuel cell (DMFC)

Methanol gets oxidized at anode of DMFC. The electrocatalytic activities for methanol oxidation for Pt/STA-C & Pt-Ru/STA-C electrocatalysts have been compared with that of Pt/C & Pt-Ru/C prepared using hydrogen reduction method. The electrocatalysts were analyzed by cyclic voltammetry in an electrolyte of 1 M H₂SO₄ and 1 M CH₃OH at 25 mV/s. The comparative voltammograms are shown in Fig. 5a and 5b respectively.

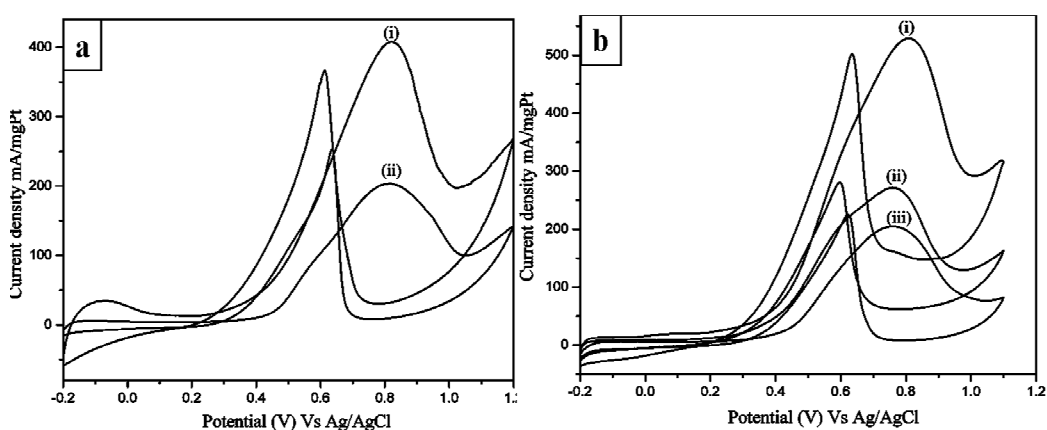


Fig. 5 Cyclic voltammograms of (a) (i) Pt/STA-C and (ii) Pt/C ; (b) (i) Pt- Ru/STA-C, (ii) Pt-Ru/ C (J. M) and (iii) Pt-Ru/C in 1M CH₃OH - 1M H₂SO₄ at a scan rate of 25 mVs⁻¹

Table 2. Comparison of electrocatalytic activities of various electrodes towards methanol oxidation

Catalyst	EAS ^a (m ² g ⁻¹)	Onset Potential (V)	I _p /I _b	Mass Activity (mA/mg ⁻¹ Pt)	Specific Activity (mAcm ⁻² Pt)
Pt/C	23.3	0.31	0.80	191	0.81
Pt/STA-C	33.0	0.21	1.11	370	1.12
Pt-Ru/C	17.2	0.21	0.91	204	1.18
Pt-Ru/STA-C	25.6	0.17	1.05	503	1.96
Pt-Ru/C (J.M)	22.5	0.17	0.95	271	1.20

The various parameters including the onset potential, mass activity (current density at 0.75V of methanol oxidation from CV per unit mass of Pt loading), specific activity (current density at 0.75 V normalized with Pt surface area) and the ratio of the

forward oxidation current peak (i_f) to the reverse current peak (i_b) of all the studied electrodes are shown in Table. 2. The mass activity for methanol oxidation follows the order: Pt-Ru/STA-C > Pt/STA-C > Pt-Ru/C (J.M) > Pt-Ru/C > Pt/C. Further, it has also been shown that the specific activity of Pt-Ru/STA-C composite (1.96 mAcm⁻² Pt) is higher than the Pt-Ru/C (1.18 mAcm⁻² Pt) and commercial Pt-Ru/C (J. M) (1.20 mAcm⁻² Pt). The experimental results highlight that the Pt/STA-C and Pt-Ru/STA-C composites show good improvement in the methanol oxidation activity.

3.5.2. Pt/STA-C as cathode electrocatalyst for DMFC

Reduction of oxygen takes place at cathode in DMFC. POMs can effectively promote the oxygen reduction reaction (ORR) in combination with Pt nanoparticles by acting as co-catalyst or promoter due to its reductive reactivity towards hydrogen peroxide intermediates that forms during electrochemical oxygen reduction reaction. Using this concept, in the present study the nanocomposites (20% Pt/STA-C) prepared has been employed as electrocatalyst for ORR. To study the efficiency of the prepared electrocatalyst (20% Pt/STA-C) for ORR, the activity has been compared with the STA free 20% Pt/C prepared by using gaseous H₂ as reducing agent. The ORR studies using linear sweep voltammetric studies for 20% Pt/STA-C and 20% Pt/C have been shown in Fig. 6 (a) and (b).

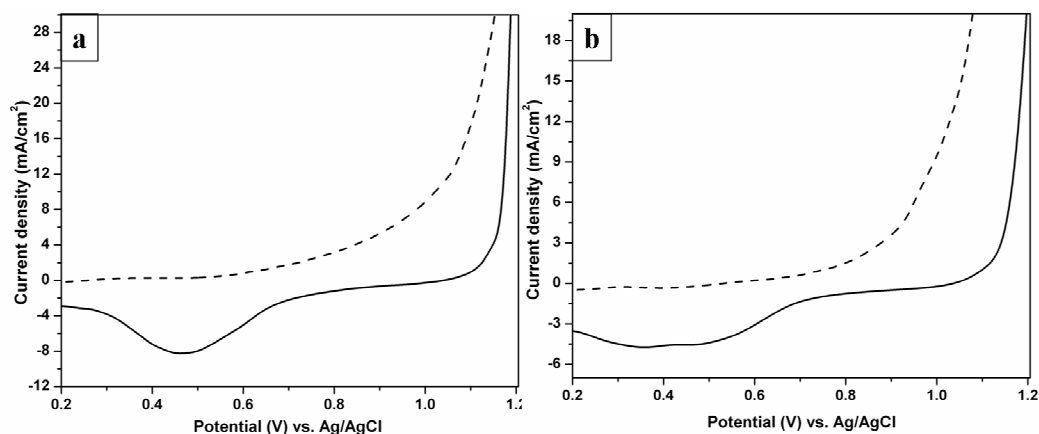


Fig. 6 Linear sweep voltammograms of (a) 20% Pt/STA-C and (b) 20% Pt/C in Ar (dashed line) and O₂ saturated (solid line) 0.5 M H₂SO₄ at a scan rate of 5 mVs⁻¹

From Fig. 6a & b, it is observed that Pt/STA-C is more active for oxygen reduction, as indicated by higher current densities at each potential in the O₂-saturated solution than those using Ar. The improved activity in the case of Pt/STA-C than Pt/C might be due to the high dispersion of Pt active sites and high electrochemical active surface area achieved by STA reduction method. The specific activity of the Pt/STA-C is greater than that of Pt/C suggested by higher current densities at a given potential, e.g.

7.59 mAcm⁻² against 4.25 mAcm⁻² at 0.5 V. This suggests the beneficial effect of STA modification on the catalyst activity towards oxygen reduction.

3.5.3. Exploitation of Ru/STA-C for electrochemical supercapacitor electrode applications

In the present study 10, 20 and 30 wt% of Ru/STA-C have been prepared and exploited for the electrochemical supercapacitor applications. STA free 20% Ru/C has also been studied and compared with the activities with Ru/STA-C composite electrodes. The existence of Keggin type POM, silicotungstic acid (STA), in the composites has enhanced the specific capacitance of the electrode. The Ru nanoparticles in all the composite samples were electrochemically oxidized to RuO₂ by sweeping the voltage from open circuit potential (≈ 0.54 V) to 0.79 V vs. Ag/AgCl (Satd KCl) and holding at 0.79 V for 2 h (Miller *et al.*, 1997; Yu *et al.*, 2006). The charge-discharge behavior of RuO₂ present in all the composites was examined by chronopotentiometry. Typical results in the potential range between 0.0 V and 0.7 V in 1.0 M H₂SO₄ solution at a current density of 3 mAcm⁻² are shown in Fig. 7. The charge-discharge profile of Vulcan XC-72R has also been compared with all the composites containing RuO₂.

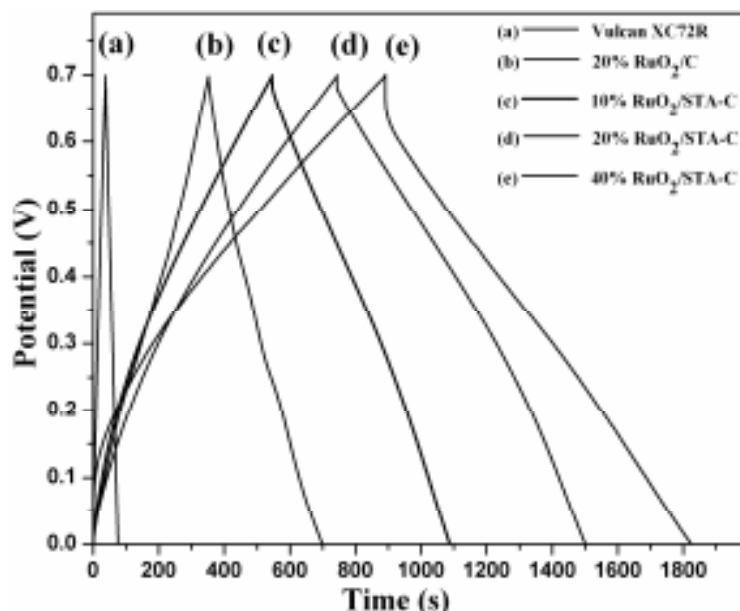


Fig. 7 Chronopotentiograms measured in 1.0 M solution between 0.0 V and 0.7 V at 3 mA cm⁻² for (a) Vulcan XC72R (b) 20% RuO₂/C (c) 10% RuO₂/STA-C (d) 20% RuO₂/STA-C and (e) 40% RuO₂/STA-C.

The specific capacitance of each nanocomposite has been evaluated using the formula

$$\text{Specific capacitance, } C \text{ (Fg}^{-1}\text{)} = i\Delta t/m\Delta V$$

where i is the current used for charge/discharge (3 mAcm^{-2}), Δt is the time elapsed for the charge or discharge cycle, m is the mass of the active electrode (7.14 mg), and ΔV is the voltage interval (0.7 V) of the charge or discharge. Specific capacitance of the Vulcan XC-72R was found to be 23 Fg^{-1} , where as, $\text{RuO}_2/\text{STA-C}$ composites exhibited higher specific capacitance values which are directly proportional to the weight percentage of RuO_2 loading (i.e., 325, 453, and 557 Fg^{-1} for 10, 20 and 40% Ru loadings in $\text{RuO}_2/\text{STA-C}$ composites). The specific capacitance of 20% RuO_2/C showed a specific capacitance of 210 Fg^{-1} . The obtained specific capacitance values show that the presence of STA in the nanocomposites has significantly improved the specific capacitance of RuO_2 present in the nanocomposites.

3.6. Preparation of metal (W and Mo) carbides by pyrolysis of Polypyrrole-POM composites

WC production generally proceeds as a two-step process. First, tungsten oxide is reduced to high-purity tungsten in a hydrogen atmosphere. The tungsten metal is then mixed with the required amount of carbon and reacts at a temperature $\sim 1400\text{--}1600 \text{ }^\circ\text{C}$ to produce tungsten carbide (Girandon *et al.*, 2000). In the present study the pyrolysis of the polypyrrole-POM composites under Ar and 95%Ar-5% H_2 lead to the formation of metal carbides (WC and Mo_2C) at $900 \text{ }^\circ\text{C}$. Polypyrrole (PPy) functioned as carbon source as it decomposes to carbon at $800 \text{ }^\circ\text{C}$ (Jang and Yoon, 2003). Phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, PW_{12}) and Phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$, PMo_{12}) have been utilized as source of POMs. The pyrolysis of PPy- PW_{12} and PPy- PMo_{12} lead to the formation of WC and Mo_2C respectively. The present preparation procedure allowed the formation of metal carbides with no addition of carbon at later stages of the synthesis as involved in conventional procedures. Fig. 8 shows the XRD patterns of WC and Mo_2C formed during the pyrolysis of polypyrrole-POM nanocomposites

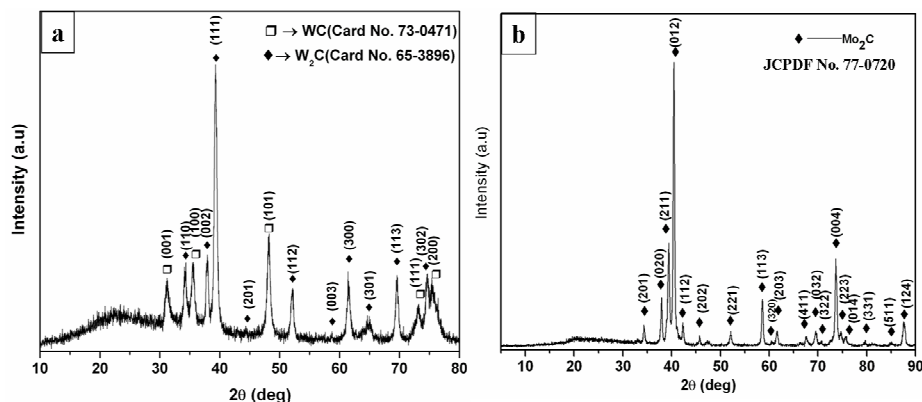


Fig. 8 XRD patterns of (a) WC and (b) Mo_2C by pyrolysis of PPy-POM composite

The prepared metal carbides have also been characterized by SEM, HRTEM and EDX analysis. Pt nanoparticles have been loaded on WC in order to study their application as electrode materials for hydrogen evolution reaction.

4. CONCLUSIONS

- POMs have been employed as catalysts and their high Brønsted acidity has been exploited for the synthesis biodegradable polymer poly(lactic acid) and fine chemical (methoxy methyl chloride)chloromethyl methyl ether) and the catalysts have shown to be more efficient than mineral acid catalysts.
- The electron transfer ability in association with strong adsorption capability of POMs has been well exploited for the development of a simple and reliable protocol for the synthesis of carbon supported metal nanoparticles-POM composites (Pt/POM-C, Pt-Ru/POM-C, Ru/POM-C and Pd/POM-C)
- The ability of Keggin type POM, $H_3PMO_{12}O_{40}$ to perform simultaneous oxidation reduction reactions has been exploited for simultaneous oxidation of aniline and reduction of metal salts for the synthesis of metal nanoparticle embedded conducting polymer nanocomposites
- Carbon supported metal nanoparticles containing POMs have been exploited for electrochemical energy conversion and storage applications. POM containing nanocomposites have shown improved performance over POM free nanocomposites.
- Metal carbides (WC and Mo_2C) have been conveniently prepared by the pyrolysis of polypyrrole-POM nanocomposites. The obtained WC has been exploited as support for the Pt nanoparticles. These materials have been used as electrocatalysts for hydrogen evolution reaction and superior performance was observed.

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Proposed contents of the thesis

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Chapter 7	Summary and Conclusions

List of publications based on research work

1. **P. S. Kishore, B. Viswanathan and T. K. Varadarajan**, (2006) Heteropolyacid catalyzed synthesis of chloromethyl methyl ether, *Tetrahedron Letters*, 47, 429- 431.
2. **P. S. Kishore, B. Viswanathan and T. K. Varadarajan**, (2008) Synthesis and Characterization of Metal nanoparticle embedded Conducting Polymer-Polyoxometalate Composites, *Nanoscale Res. Lett.*, 3, 14-20.

Other Publications

1. **J. Rajeswari, P. S. Kishore, B. Viswanathan, T. K. Varadarajan** (2007) Facile hydrogen evolution reaction on WO₃ nanorods, *Nanoscale Res. Lett.*, 2, 496-503.

Patents Filed

1. **D. V. Ramana, P. S. Srinivasan, T. Prakasam, B. Viswanathan, T. K. Varadarajan, S. Shanmugam and P. S. Kishore** (2008) An improved process for

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List of conferences

1. **P. S. Kishore, B. Viswanathan and T. K. Varadarajan** (2006) Oral presentation on "Generation of Pt/C and Pt-Ru/C electrocatalyst in the presence of polyoxometalates" in *Taiwan- India conference on nanomaterials*, December 11-12, Department of Materials Engineering, Lunghwa University of Science and Technology, Taiwan.

2. **P. S. Kishore, B. Viswanathan and T. K. Varadarajan** (2006) Poster presentation on "One pot synthesis of polypyrrole - silver nanoparticle composites by using polyoxometalates as redox switch" in *International Conference on Nanomaterials and its Applications*, February 4-6, Department of chemistry, NIT Trichy, India.

3. **P. S. Kishore, B. Viswanathan and T. K. Varadarajan** (2007) Oral presentation on "Recent attempts in the development of Biodegradable polymers based on Polylactic acid (PLA)" in National seminar on application oriented materials (NSAOM), August, Rajyalakshmi Engineering college, Chennai, India.

4. **P. S. Kishore, B. Viswanathan and T. K. Varadarajan** (2008) Poster presentation on "Electrochemical oxygen reduction reaction by Pt nanoparticles on Carbon support stabilized by polyoxometalates" in International Conference on Nanoscience and Technology (ICONSAT), February 27-29, held by Nanomission, Department of Science and Technology, Chennai, India.