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  15. This diastereomeric purity was also confirmed by direct comparison of **11** with *anti* selective aldol products<sup>11</sup> (*anti* : *syn* = 3 : 1) from 4-methylvaleric acid and 3-benzoyloxypropanal using <sup>1</sup>H-NMR.
  16. Spectral data for **12**: mass spectrum (EI) *m/z* 278 (M<sup>+</sup>, 2.3), 216 (4.2), 128 (10.9), 91 (100); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 0.88 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H), 1.40 (m, 3H), 1.91 (m, 2H), 3.60 (dd, *J* = 9.2, 7.5 Hz, 2H), 4.20 (m, 1H), 4.52 (s, 2H), 4.78 (m, 1H), 6.90 (br s, NH), 7.34 (m, 5H).

## Studies on the Electron Transfer at Semiconductor Electrodes by Surface Modification: 1. Catalytic Activity of Iron-Substituted Heteropolytungstate Ions at Polyvinylpyridine Modified Electrode

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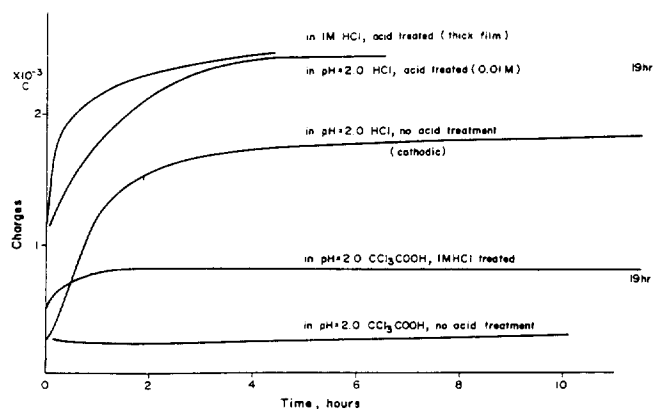
Electrodes coated with thin polymers and polyelectrolytes in which redox sites are incorporated have become one of the most preferred approaches for the construction of polymer modified electrode surface because of its simplicity.<sup>1</sup> The concept of chemically modified electrode is borne out to control the chemical nature of the electrode surface. By deliberately attaching chemical reagents or "tailor-made type" functionalities onto the electrode, the electrode would take on the chemical properties of the attached reagents. Potential applications in electrocatalytic reactions have provided much of the incentive for this development as in the case of the reduction of oxygen in Nafion coated electrode.<sup>2</sup> Methods for immobilizing chemical reagents on electrode surfaces are well characterized elsewhere.<sup>3</sup>

The most extensively used polymer films are polyelectrolyte type with electric charges on them; they are protonated or quaternized poly(4-vinyl pyridine)(L-polylysine),<sup>1c</sup> sulfonated or carboxylated fluoropolymers(Nafion),<sup>4</sup> protonated poly(4-vinyl pyridine),<sup>5,6</sup> random ternary copolymers,<sup>7</sup> poly(styrenesulfonate),<sup>8</sup> and cationic perfluoropolymers.<sup>9</sup> Requirements of such polyelectrolytes are strong, irreversible binding or adsorption to the electrode surface, reasonable ion-exchange capacities, retention of counter ionic reactants for long periods, rapid charge propagation rates within the coatings and reasonable chemical and mechanical stability. Theoretical analysis of the mechanisms and kinetics of charge propagation within polymer and polyelectrolyte coatings have been reported.<sup>10</sup>

Oxometalate ions which are composed entirely with inorganic elements have shown distinctive properties, especially when a transition element is substituted.<sup>11</sup> Electrochemical and electrocatalytic properties of iron-substituted heteropolytungstate ion in aqueous media were extensively studied by Toth and Anson.<sup>12</sup> Several efficient ways of immobilization or anchoring isopoly and heteropoly oxometalates on various supports have been demonstrated.<sup>13</sup>

This communication examines the possibility of entrapping iron-substituted heteropolytungstate ions into protonated PVP matrix and shows their electrochemical and electrocatalytic properties of the entrapped ions.

Preparation of polymer-coated electrodes was partly following the literature.<sup>5</sup> A stock solution of 0.5% poly(4-vinyl pyridine)(Polyscience) was prepared by dissolving PVP in 2-propanol. A solution of 0.755 mM of 1,12-dibromododecane (Aldrich) in the same solvent was prepared. Equal volumes of these two solutions were mixed and then 1-2 microliters of the mixture were applied on the polished glassy carbon



**Figure 1.** Time variation of charge from the first wave during the incorporation of  $\text{SiW}_{12}\text{O}_{40}^{4-}$  into PVP.  $[\text{SiW}_{12}\text{O}_{40}^{4-}] = 5 \text{ mM}$ .

(GC-30, Tokai, Japan, area =  $0.22 \text{ cm}^2$ ) surface and evaporated at room temperature. The film coated electrodes were maintained at  $80^\circ\text{C}$  in a vacuum oven for 18 h to promote the cross-linking reaction between the alkyl halide and pyridine residues. Degrees of cross-linking reaction were controlled by varying the volume ratios of the solution. Heteropolyanions were incorporated into the coating electrostatically either by cycling the potential between  $+0.3$  and  $-0.85 \text{ V}$  vs SCE in  $5 \times 10^{-3} \text{ M}$  aqueous solution of heteropolyanions in  $0.1 \text{ M}$  electrolyte or by immersing the electrode in the same solution for more than two hours. Electrochemical measurements were made with modified electrodes in a given supporting electrolyte solution after the electrode surface was thoroughly rinsed with distilled water. The Keggin-type of 12-tungstosilicic ion,  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$  ( $\text{SiW}_{12}$ ), its lacunary ion,  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  ( $\text{SiW}_{11}$ ), and iron-substituted ion,  $[\text{Fe}(\text{II})\text{SiW}_{11}\text{O}_{39}]^{5-}$  ( $\text{FeSiW}_{11}$ ), were used for incorporation.

The current growth due to the electrochemical behavior of three heteropolytungstate ions by successive cycling in the loading stage can be observed as in any polymer modified electrode.<sup>3b,9</sup> Shapes of cyclic voltammogram of three heteropolyanions are roughly the same as those obtained from the solution. The charge obtained from the first reduction wave of  $\text{SiW}_{12}$  is plotted in Figure 1. It shows the variation of charge with time for electrodes with or without acid treatment (soak PVP film coated electrodes in  $1 \text{ M}$  or  $0.01 \text{ M}$  HCl for 2 h) in  $\text{CCl}_3\text{COOH}$  or HCl solution of pH 2.0 containing  $\text{SiW}_{12}$ . The incorporated amount strongly depends on the status of the electrode and the electrolyte employed. The amount of loading in  $\text{CCl}_3\text{COOH}$  without acid treatment is less than 10% of the largest value obtained with the electrode that has been soaked in HCl and then incorporated in  $0.01 \text{ M}$  HCl solution. Generally, acid-treated electrodes show more loading than the ones without treatment. This observation is different from the results of Keita *et al.* where the same maximum amount of loading can be obtained in 26 h in  $\text{CF}_3\text{COOH}$  (pH = 1.5) even without acid treatment.<sup>13b</sup> This is probably due to the different geometric structure of polymers employed in both studies. The morphology of PVP coatings must be different whether the film is exposed to acid before loading or it is exposed to acidic solution containing oxometalate. This is why acid-treated films always exhibit more loadings than the one without acid treatment

**Table 1.** Formal Potentials of Heteropolyanions in Solution and in PVP Film

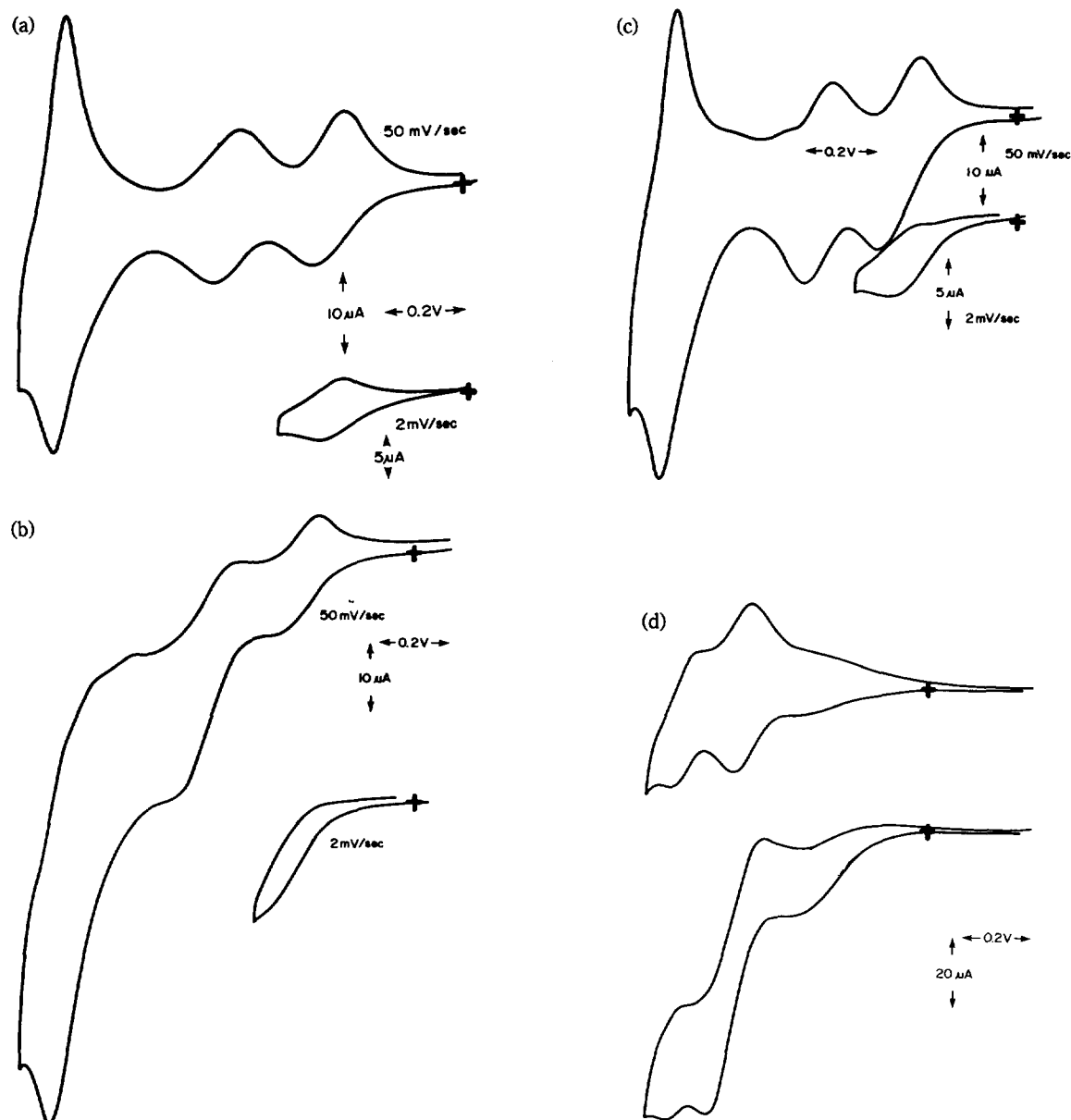
Heteropolyanions	$-E^f$ (V)		Ph dependence film (mV/pH)	
	Solution	Film		
$\text{SiW}_{12}\text{O}_{40}^{4-}$	1st 1-e wave	.245	.150-200	~30
	2nd 1-e wave	.525	.450-510	
	3rd 2-e wave	.770	.790-810	
$\text{SiW}_{11}\text{O}_{39}^{8-}$	1st 2-e wave	.540	.500-560	~60
	2nd 2-e wave	.760	.690-770	
$\text{FeSiW}_{11}\text{O}_{39}^{5-}$	Fe wave	.050	.150-250	~30
	1st 2-e wave	.565	.510-540	~60
	2nd 2-e wave	.670	.700-800	~60

$E^f$  vs. SCE, measured in pH = 2.0 solution of HCl + 0.1 M NaCl.

in this work. Even a less amount of loading is observed when the incorporation is made in  $0.1 \text{ M}$   $\text{CH}_3\text{COOH}$  solution at pH of 4.7. Generally, HCl treatment can produce extensive protonation of pyridine groups in PVP that provide more cationic sites for accommodating anions. Quaternization or protonation of pyridine groups in the polymer that is directly related to a charge density within the PVP affects not only on the incorporation rate, but also on the amount of incorporated heteropolyanions. The amount of  $\text{SiW}_{12}$  which is incorporated into PVP film is determined to be  $0.5 \times 10^{-9}$  to  $6 \times 10^{-9} \text{ mol/cm}^2$ . Yet the maximum loading has utilized only up to about 26% of all pyridinium sites. This inefficient utilization is presumably due to the geometric hindrance from the cross-linked structure of polymer and large charges on the anion even though tungsten distributed quite evenly throughout the film. The surface morphology of the modified electrode and the distribution of oxometalates were studied by Keita *et al.*<sup>14</sup> They found that tungsten could be detected essentially in the polymer-covered areas by SEM and elemental microprobe analysis.

The formal potentials of heteropolytungstate ions from solution and from modified films are listed in Table 1. All potential values are referenced against SCE. A minor difference in the shape and potential are observed. One of the main variations in potential is in waves from  $\text{SiW}_{12}$  and  $\text{FeSiW}_{11}$ . The formal potentials of the first two waves shift to positive direction, while the third reduction wave ( $E^f \sim -0.75 \text{ V}$ ) exhibits negative shift. The pH dependence of the second and third waves ( $E^f \sim -0.5$  and  $-0.75 \text{ V}$ ) is around  $60 \text{ mV/pH}$  indicating the addition of the same number of protons and electrons in the reduction, while the first waves show about  $30 \text{ mV/pH}$ . About  $60$  to  $90 \text{ mV/pH}$  was observed in solution for the last two waves.<sup>12a</sup>

The relative peak currents from the second wave from oxometalate frame work are quite different from the ones obtained from solution. It seems the relative size of the peak current is a strong function of the electrolyte, which is a good indication of electrostatic repelling or attraction of anions, that plays a key role in the electrochemical process in addition to charge hopping, to balance the charge unbalance occurred during the electrochemical reaction.<sup>13b</sup> Unusual stability of the incorporated PVP film has been experienced especially in the case of  $\text{SiW}_{12}$ . Similar stability has also been



**Figure 2.** Electrochemical behavior of  $\text{FeSiW}_{11}\text{O}_{35}^{5-}$  attached PVP. The small lower curves were obtained with the scan rate of 2 mV/s while the main curves were with 50 mV/s. The origin is marked in each curve. (a) In deaerated 0.1 M NaCl solution (pH=2.0); (b) In  $\text{O}_2$  saturated solution; (c) In 1 mM  $\text{H}_2\text{O}_2$  solution; (d) The upper curve is obtained in solution without  $\text{NO}_2^-$  and the lower curve is in the presence of 1 mM  $\text{NO}_2^-$ .

obtained with other heteropolyanions except iron substituted ones.<sup>13</sup> Chemical reaction in the polymer matrix was suspected.<sup>13c</sup>

Catalytic activities toward the reduction of oxygen, hydrogen peroxide and nitrite ion are noted as shown in Figure 2. Only  $\text{FeSiW}_{11}$  displays the electrocatalytic property while  $\text{SiW}_{12}$  nor  $\text{SiW}_{11}$  shows little effect on those reactions. Not only the reduction occurs at more positive potential, a large cathodic current flows where iron wave appears. The anodic scan especially at rather slow scan rate (2 mV/s) shows no current because  $\text{Fe(II)SiW}_{11}$  is exhaustively oxidized by the catalytic reaction. Similar catalytic behavior was obtained in the homogeneous solution phase.<sup>12</sup> Catalysis by redox media-

tor couples attached to the electrode surface has the advantage over homogeneous catalyst in which smaller quantities of catalyst are needed and cumbersome separation problems are avoided. Details of the electrocatalytic property will be published later.

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## A New Catalyst System for the Aldol Type Condensation of Silyl Enol Ethers and Ketene Silyl Acetals

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The aldol reaction is one of the most fundamental and important carbon-carbon bond formation reaction in organic synthesis. In 1973, the reaction of carbonyl compounds with silyl enol ether promoted by Lewis acid such as  $\text{TiCl}_4$  was reported for the first time<sup>1</sup>. Over the years, so much effort has been devoted to the development of catalysts which efficiently promote the coupling reaction of carbonyl compounds with silyl carbon nucleophiles that various catalysts were developed for example, trityl cation<sup>2</sup>, fluoride ion<sup>3</sup>,  $\text{BiCl}_3$ <sup>4</sup>, phosphonium salts<sup>5</sup>, and various lanthanide salts<sup>6</sup>.

In the course of our investigation to explore new catalyst, a novel catalyst system,  $\text{TMSCl-InCl}_3$ , was developed for the reaction of O-trimethylsilylmonothio acetals with triethyl silane and some silyl carbon nucleophiles. But, this catalyst was not so effective for the reaction of carbonyl compounds with silyl carbon nucleophiles<sup>7</sup>. Therefore it was necessary to develop more effective catalyst for the aldol type reactions.

We screened some combination of weak Lewis acids ( $\text{InCl}_3$ ,  $\text{SnCl}_4$ ,  $\text{ZrCl}_4$ ,  $\text{SbCl}_3$ , and  $\text{SiCl}_4$ ) and metal salts ( $\text{AgClO}_4$ ,  $\text{LiOTf}$ ,  $\text{AgOTf}$  and  $\text{AgSbF}_6$ ) in the reaction of benzaldehyde and 1-trimethylsilyloxy-1-cyclohexene. From this results, the combined use of  $\text{InCl}_3$  and  $\text{AgClO}_4$  is most effective for coupling reaction than any other combinations. Although  $\text{InCl}_3$  itself has a poor activity as promoter, the combined use of  $\text{InCl}_3$  with the equimolar amount of  $\text{AgClO}_4$  gave rise to the impressively rapid and clean reaction. Until now, some catalyst system,  $\text{TrClO}_4$ <sup>2</sup>, and  $\text{Cp}_2\text{MCl}_2\text{-AgClO}_4$ <sup>8</sup> ( $\text{M} = \text{Ti, Zr, Hf}$ ) were used in the aldol reaction or glycosidation reactions. But, as far as we know,  $\text{InCl}_3\text{-AgClO}_4$  catalyst system was used in the aldol reaction by us for the first time.

Reactions of benzaldehyde and 3-phenylpropanol with some silyl enol ethers and ketene silyl acetals in the presence of  $\text{InCl}_3\text{-AgClO}_4$  catalyst system (10 mol%) are demonstrated in Table 1.

In all cases, the reactions proceeded smoothly at low temperature and the corresponding aldol adducts were obtained in fairly good yields.

In conclusion, the combination of  $\text{InCl}_3\text{-AgClO}_4$  is shown to be an effective catalyst for the aldol type carbon-carbon bond forming reaction of aldehydes with various silyl nucleophiles. The application of this catalyst to the other reactions are underway.

Typical procedure: Indium (III) chloride (0.03 mmol) was placed in a 30 ml flask and dried *in vacuo* by heating for