

Feasibility of the Redox Sulfur Recovery Process using Heteropoly Molybdophosphate

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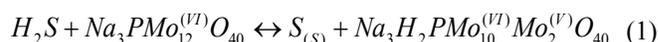
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Abstract: The feasibility of the removal of sulfide species using acid solutions of 12-molybdophosphoric acid was studied. The key factor in this purification process is the formation of a hydrogen-bonded structure between the hydrogen sulfide species and the bridging oxygen atom of the MoO₆ octahedrons of the molybdophosphate complexes. The number of bridging oxygen atoms depends of the pH. Consequently, the efficiency of the process is also largely dependent on the pH. Most of the literature focuses on the redox potentials for the purification process. The slope of the redox pair S/H₂S and the molybdophosphate complexes is -59 pH/mV. The differences between the redox potentials do not fluctuate with the pH, which indicates that the oxidation of H₂S by molybdophosphate complexes is spontaneous in all pH intervals but does not explain why the efficiency decreases at high pH. In summary, the Keggin-type structure contributes to the efficient removal of sulfide because this structure contains the maximum number of bridging oxygen atoms. The solubility of H₂S gas is lower in acidic media. This drawback severely restricts the performance of the purification process.

Keywords: 12-Molybdophosphoric, Phosphomolybdic acid, Removal of sulfur compounds, Hydrogen Sulfide

1. INTRODUCTION

Electrochemical processes for the removal of H₂S are divided into two groups: direct electrochemical reactions of sulfur compounds at the electrode [1–5] and indirect processes that utilize electrochemically regenerated redox mediators as the oxidizing agent [6]. Ogutveren [7] and Kelsall [8] reviewed the literature available up to 2013 and suggested possible routes for future research. In particular, the electrochemical production of hydrogen with simultaneous sulfur oxidation was highlighted. Ogutveren [7] concluded that the indirect processes is the closest to development for commercial applications. On the other hand, Pope [9] and Weinstock [10] reviewed studies that proposed the formation of elemental sulfur from the reaction of H₂S or HS with several types of polyoxometalates. There are two studies that use 12-molybdophosphoric acids or salts for the removal of sulfur compounds. Zhao [11] investigated the removal of H₂S from gas streams with a solution of 12-molybdophosphoric acid. Wang [12] postulated reaction (1) between H₂S and sodium phosphomolybdate:



The work of Kim, Song and Han [13] was presented as an original contribution because it proposed a system that coupled an adsorption column with a fuel cell to regenerate the adsorption media. The purification process is illustrated in a schematic diagram in Fig. 1. However, some interpretations of their results need to be revised, including the redox potential determination of the phosphomolybdate species. Our study is expected to contribute to the interpretation of the results of Kim, Song and Han [13]. Consequently, our search was conducted to determine the feasibility of the sulfur removal process using 12-molybdophosphoric acid.

2. MATERIALS AND METHODS

2.1. Speciation Diagrams

A speciation diagram shows the relative abundance (α_A) of species A versus the pH and is defined by the relationship:

$$\alpha_A = \frac{[A]}{C_t} \quad (2)$$

where $[A]$ is the concentration of species A , and C_t is the total

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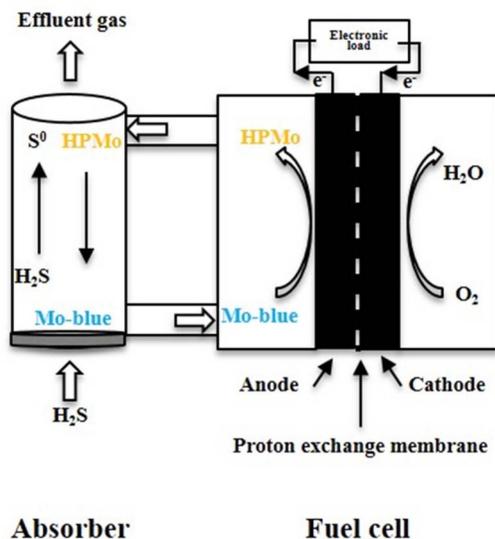


Figure 1. Schematic representation of the purification process proposed by Kim, Song and Han [13].

concentration of all of the species that contain species A , as defined by the material balances in equation (3):

$$C_i = [S^{2-}] + [HS^-] + [H_2S] \quad (3)$$

For example, the equation for the α -fraction of S^{2-} is as follows:

$$\alpha_{S^{2-}} = \frac{[S^{2-}]}{[S^{2-}] + [HS^-] + [H_2S]} \quad (4)$$

The α -fraction for a specific species can be calculated by substituting the equilibrium constants into the equation of the α -fraction. For example:

$$\alpha_{S^{2-}} = \frac{1}{1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1 K_2}} \quad (5)$$

where $[H^+]$ denotes the proton concentration, and K_1 (6) and K_2 (7) are the equilibrium constants of reactions (8) and (9), respectively [14].

$$K_1 = 10^{-6.97} = \frac{[H^+][HS^-]}{[H_2S]} \quad (6)$$

$$K_2 = 10^{-12.92} = \frac{[H^+][H^{2-}]}{[HS^-]} \quad (7)$$



Equations (2) to (9) were used to draw the speciation diagram in Fig. 2, which is discussed in Section 3.

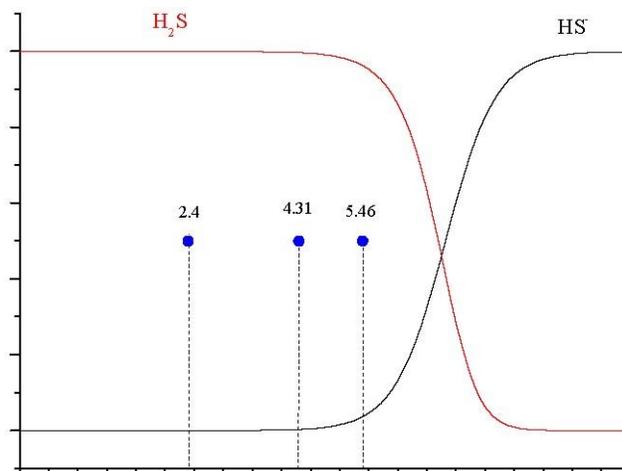
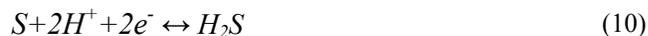


Figure 2. Speciation of the sulfide species as a function of pH. H_2S (—) and HS^- (—). The concentration of S^{2-} was negligible at pH values less than 7 and therefore was not indicated in the diagram. The dashed lines (----●) indicate the pH jumps determined by Reddy [18].

2.2 Nernst Equations

The potentials of electrode reactions (10) and (11) are expressed in terms of the concentrations and standard potentials using the Nernst equations (12)-(13) [15].



$$E = 0.174 - 0.05916 \text{ pH} - 0.02958 \log [H_2S] \quad (12)$$

$$E = 1.229 - 0.059 \text{ pH} \quad (13)$$

The concentrations, or activities, of the aqueous sulfate and sulfide anions were considered to be unity. Equation (12) was used to draw the slopes in Fig. 4, which is discussed in Section 3.

2.3. The Mid-peak Potential

The Mid-peak potential in cyclic voltammetry is a quantity calculated by the following equation:

$$E_{\text{Mid-peak}} = \frac{E_{pa} + E_{pc}}{2} \quad (14)$$

where E_{pa} is the anodic peak potential and E_{pc} is the cathodic peak potential [16]. The Mid-peak potentials are included in Fig. 4.

2.4. Cyclic voltammetry

All reagents were of analytical grade, were acquired from commercial sources and were used without further purification. Sulfuric acid (98.08%) was purchased from J.T. Baker (USA), Nafion® 5% ethanol was obtained from ElectroChem (USA), high-purity N_2 gas was purchased from Infra Praxair (México), and solid phosphomolybdic acid was purchased from Sigma-Aldrich (USA). Glassy carbon was provided by BAS (USA). The electrolyte H_2SO_4 was prepared with water from a Millipore -Milli-Q Plus. An Autolab Model PGSTAT 302 potentiostat (Netherlands) was used to per-

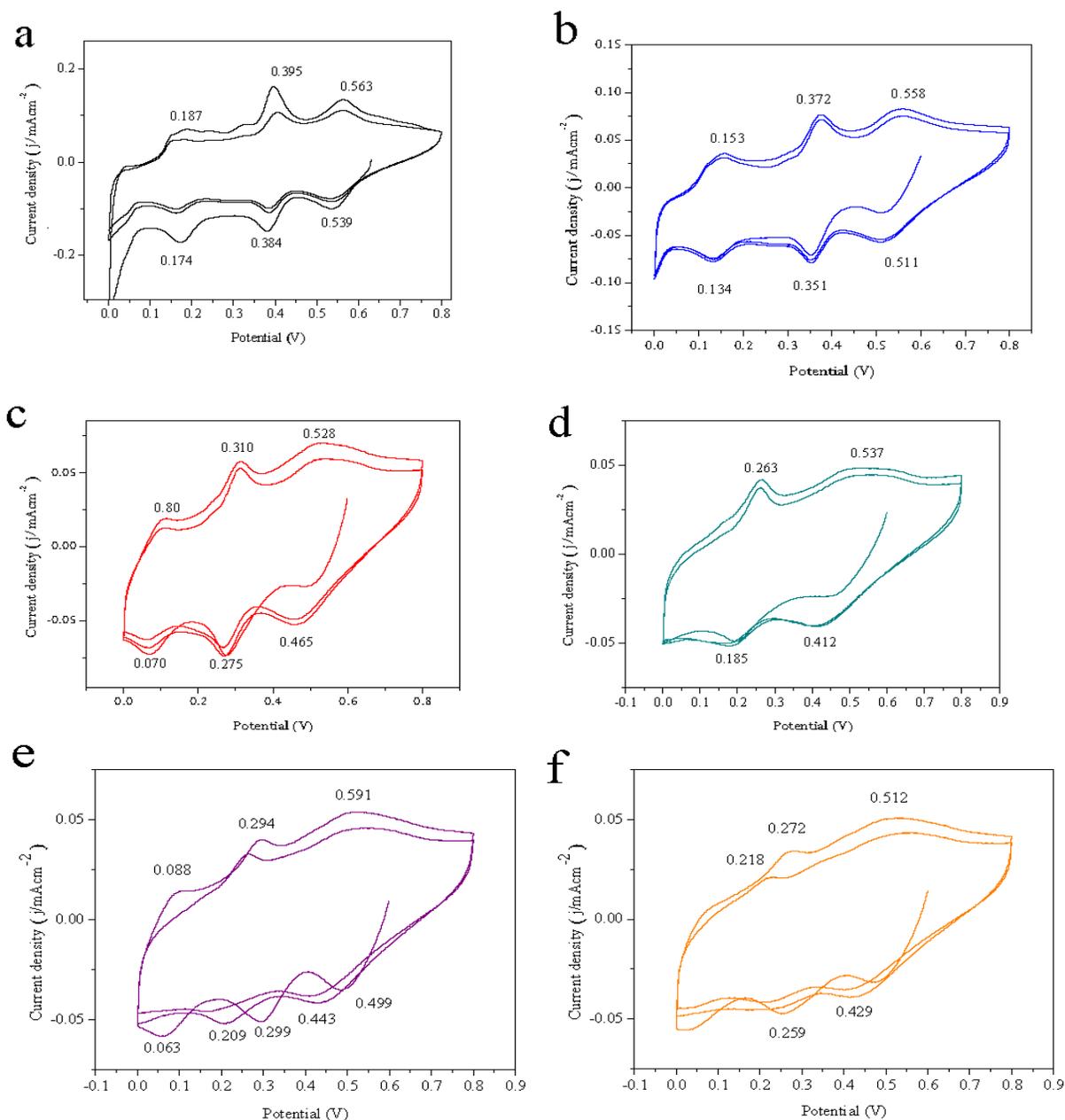


Figure 3. Cyclic voltammograms of molybdophosphoric acid immobilized in Nafion and deposited on a glassy carbon electrode. The scan rate was 10 mV s⁻¹, and the pH values were a) 0.34, b) 1.06, c) 2.02, d) 3.09, e) 4.12 and f) 5.91.

Table 1. Comparison of the pH jumps determined by Reddy [18] and the pKas of the lacunary species reported by Pettersson [20]. The standard deviation in each row measures the relative spread of the values of the pH jump with respect to the pKa values.

lacunary species	pKa	pH-jump	Standard deviation
$Mo_5P_2O_{23}^{6-} / HMo_5P_2O_{23}^{5-}$	5.10	5.46	0.2546
$HMo_5P_2O_{23}^{5-} / H_2Mo_5P_2O_{23}^{4-}$	3.79	4.31	0.3677
$Mo_9PO_{31}(OH_2)_3^{3-} / Mo_9PO_{31}OH(OH_2)_3^{4-}$	2.46	2.40	0.0424
$Mo_{11}PO_{39}^{7-} / HMo_{11}PO_{39}^{6-}$	4.42	4.31	0.0778
$HMo_{11}PO_{39}^{6-} / H_2Mo_{11}PO_{39}^{5-}$	2.95	2.40	0.3889

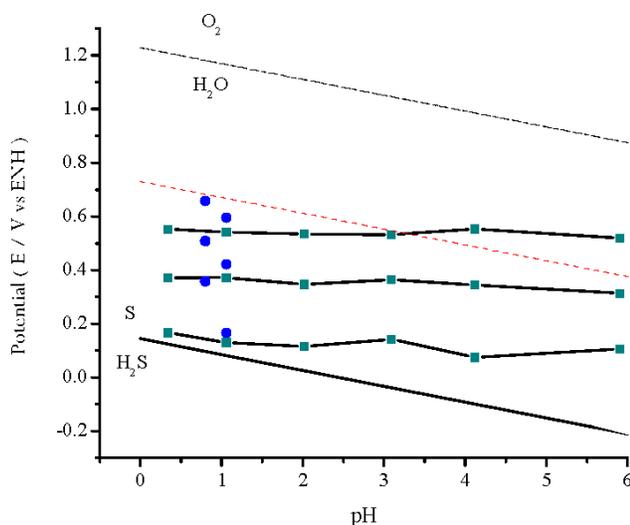


Figure 4. The mid-peak potentials of the molybdophosphoric acid and molybdophosphate complexes (—■—) calculated with equation (14) from the data in Fig. 3. The potential of the redox pair H_2S/S (—) and O_2/H_2O (----) calculated using the Nernst equations (11) and (13), respectively. The symbol (●) indicates the anodic peaks potentials reported in [13], and the dashed line (----) is the slope of -59 mV /pH reported by Sadakane [24].

form voltammetry. An $Hg|Hg_2SO_4|K_2SO_4$ electrode was used as the reference electrode, and a platinum wire (99.99%) in a spiral shape was used as the counter electrode. All potentials are given versus a reversible hydrogen electrode (RHE).

The glassy carbon electrode was polished with alumina to obtain a mirror surface. Liquid Nafion ink was used to deposit the phosphomolybdic acid on the glassy carbon electrode (GCE). The liquid ink was prepared as follows: 4 mg of phosphomolybdic acid powder was dissolved in 1 mL of ethanol, and 5 μ L of this solution (2.2 mM phosphomolybdic acid) was mixed with 5 μ L of Nafion. The resultant liquid ink was sonicated for 5 minutes. Then, using a micropipette, 5 μ L of the liquid ink was placed on the surface of the polished GCE. Before immersing the GCE/Nafion electrode, the experimental solutions were deoxygenated by bubbling with N_2 gas (99.9% purity). All experiments were performed twice.

To change the pH of the solutions, H_2SO_4 was added dropwise to a concentrated NaOH solution until the desired pH was obtained. The pH of the solutions was measured using a pH glass electrode and a digital Hach pH meter (USA).

3. RESULTS

The acid strength determination of polyoxometalates in terms of pKa is challenging [17]. In particular, for molybdophosphoric acid in aqueous solutions, protonation and deprotonation proceed through three major stages at pH levels of 2.40, 4.31 and 5.46. As a result, the titration curve of molybdophosphoric acid is characterized by three pH jumps. Reddy et al. [18] investigated these protonation processes but did not identify the species in solution during each phase. McGarvey and Moffat [19] used nuclear magnetic resonance spectroscopy (NMR) to identify the species. In their study, three signals were observed at three pH values, which corre-

late highly with the features of the titration curve. The observed signals resulted from chemical changes in the structure of the molybdophosphoric acid, and three principal species were postulated for each pH region. However, other works that attempted to identify these species produced different results [20–22]. Table 1 lists the three pH jumps and the pKas of some lacunary species reported by Pettersson [20]. Some of the pKa values are very close to the pH jumps of the titration curve, which suggests that the jumps were produced by three different species, for example, $PMo_{11}O^{3-}_{37}$. However, it is difficult to assign each pH jump directly to the protonation of a particular lacunary species because of the aforementioned disagreement of the previous studies [19–22]. Nevertheless, in all studies, the Keggin-type complex was predominant at pH 0.8, and this molecular structure is the major reactive species responsible for the remarkable degradation of sulfur species observed in [13]. The speciation diagram in Fig. 2 shows that H_2S was predominant in the pH studies performed by Kim et al. [13]. Additionally, the pKa in Fig. 2 suggests that H_2S could react with three different phosphomolybdate species depending on the pH value. Kim, Song and Han [13] recorded voltammograms at different pHs; a more complete survey of the voltammograms obtained here is detailed in Fig. 3. At a pH less than 1.5 (Fig. 3a–3b), three redox pair peaks are observed and are assigned to the following reactions [23–24]:



According to the speciation studies in [19–22], the fraction of $PMo_{12}O^{3-}_4$ is very small at pH values greater than 1.5. The peaks in Fig. 3c–3f are associated with the redox pairs of the lacunary species, including $P_2Mo_{18}O^{6-}_{62}$. The lacunary species are derived from plenary Keggin-type anions by the removal of one MoO_6 unit; consequently, the electrochemical reactions are different from reactions (15) to (17). Keita and Nadjo [25] reviewed the electrochemistry of these lacunary species, and Song and Barteau [26] mapped their reduction potentials at pH 3.1. These studies established that the transition metal centers of the lacunary species are the active sites of the electrocatalytic reactions because these centers contain the acceptor and donor orbitals of $Mo(VI)$ and $Mo(V)$, respectively. Sadakane [24] commented that it is difficult to obtain well-defined redox waves for $PMo_{12}O^{3-}_4$ by cyclic voltammetry in aqueous media. Consequently, in our experiments, molybdophosphoric acid was first immobilized in Nafion matrices on the electrode surface. Therefore, the potentials in Fig. 3 were different from the potentials of species dissolved in aqueous solution [13] (see squares (■) and circles (●) in Fig. 4). In addition to increasing the bulk pH and consequently decreasing the proton concentration, Nafion provides a more rapid and continuous supply of protons to the surface of the carbon electrode, which explains the difference of the potentials reported in Fig. 3 and [13]. The currents and peaks decrease in all of the second voltammetry cycles (---), but the peak potentials only shift at high pH values, which indicates that the proton concentration near the coated electrode is greater than in the bulk concentration. Therefore, the potentials are likely overestimated. Kim, Song and Han [13] did not report mid-peak potentials; thus, a comparison of the slopes of the lines presented in Fig. 4 is not possible. However, the pH-dependence of the electrochemical

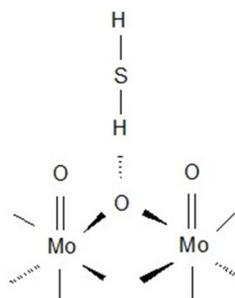


Figure 5. Scheme of the structure of the hydrogen bonds between hydrogen sulfide and the bridging oxygen atom of the MoO_6 octahedron of molybdophosphate complexes. The scheme was adapted from [10].

behavior of heteropolyacids has been observed often for both dissolved and immobilized species [24,27-30]. The low magnitudes of the slopes (mV/pH) in Fig. 4 suggest minimal dependency of the redox potentials of the lacunary species on the pH because the Nafion maintains a high proton concentration in the electrode surface region. Conversely, the line based on equation (12) has a larger slope (59 mV/pH). These negative slopes indicate that redox-type reactions resulted in the oxidation of sulfur compounds by the Keggin-structure or lacunary species. It is difficult to determine the mid-peak potentials from the data presented by Kim, Song and Han [13]; however, their voltammograms suggest that the oxidation of sulfur compounds is thermodynamically spontaneous.

Kim, Song and Han [13] supposed a dependence of the redox potential of the sulfide on the pH. This assumption was based on the experimental work of Wang [12], who measured these redox potentials in solutions with a pH between 5 and 12. Consequently, the potentials of the redox pair S/H_2S were assigned incorrectly, that is, Fig. 2 shows that the predominant species in the pH range studied by Wang [12] is HS^- , and the potential corresponds to the redox pair HS^-/S and not to the pair S/H_2S . Therefore, the redox potentials are missing in the work of Kim, Song and Han [13]. Nonetheless, in Fig. 4, slopes and the Nernst equation (12) predict that H_2S can be oxidized spontaneously to S by lacunary species. Kim, Song and Han [13] claimed that the potential difference between species explains the efficiency of the purification process. These authors postulated that this difference varies with pH, consequently altering the efficiencies. The slope of the redox potential of S_0/H_2S is -59 mV/pH (equation (12)), and the slope of HPMo/Mo-blue in solution reported by Sadakane [24] is also -59 mV/pH (see dashed line (----) in Fig. 4). The identical slopes of these redox pairs indicate that the difference between redox potentials does not fluctuate with pH. In addition, the potential differences explain the thermodynamic feasibility but not the performance. To be precise, the difference between the Nernst potentials of the redox couples indicates whether the reactions can occur spontaneously but does not indicate the reaction rate.

Fig. 4 shows the linear dependency of the redox potentials on the pH, and Sadakane [24] proposed that the slope follows the theoretical value of -59 mV/pH for a $2e^-/2H^+$ redox process (see reactions (15) to (17)), which implies that the Keggin-structure and lacunary species contain equivalent numbers of transition metal centers that can act as acceptors or donors of electrons.

Tytco [31] studied the structure and bonding of polyoxometalates using the bond valence approach. This author considered that the protonation of the bridging or terminal oxygen atoms must comply with the bond length-bond valence relationship. In this scenario, protonation of the terminal oxygen atoms in the respective MoO_6 octahedron causes appreciable changes in the bond lengths and the metal valence. Conversely, protonation of the bridging oxygen atom leaves the MoO_6 octahedron unaltered; as such, no change in the bond characteristics is expected. In this regard, Weinstock [10] commented that the ratelimiting step involved the hydrogen-bonded structure formed between the hydrogen of H_2S and the bridging oxygen atom of the MoO_6 octahedron (see Fig. 5). Under these circumstances, the high performance observed at pH 0.8 by Kim, Song and Han [13] is produced because the quantity of bridging oxygen atoms is superior in the Keggin-type structure relative to the lacunary species. When Kim, Song and Han [13] increased the concentration of $PMo_{12}O_{43}^{3-}$, the number of bridging oxygen atoms simultaneously increased. Then, the degree of sulfide removal significant increased.

The speciation diagram in Fig. 2 shows that H_2S has a large stability region from 0.8 to 5.5 pH, and the S_0/H_2S redox couple is predominant in this pH interval (Fig. 4). Consequently, H_2S can donate electrons to form elemental S (reaction (10)). The redox reaction is preceded by hydrogen-bonding interactions between the H_2S and bridging oxygen atoms of the Keggin-type structure (Fig. 5).

The discussion in previous paragraphs assumed that the purification process occurred in a homogeneous phase because Na_2S can be added to the solutions as an impurity. However, when H_2S gas was added as an impurity, the absorption efficiencies decreased because under acidic conditions, the solubility of H_2S gas is one order of magnitude lower than it is in neutral pH solutions [8]. In this case, the absorption efficiencies observed at the experimental pH values in [13] are determined by the rate of the mass transfer in a two-phase system. This situation does not invalidate the previous discussion about the catalytic activity and the formation hydrogen bonds in Fig. 5.

Kim, Song and Han [13] postulated that the Keggin-structure could be regenerated by a fuel cell containing Nafion as the electrolyte, in which the cathode reduces oxygen (11) and the anode oxidizes molybdophosphate complexes by reactions (15) to (17).

The corresponding Nernst equation (13) shows that the potentials of this reaction vary from 1.2 V (pH 0) to 0.94 V (pH 5) in the experimental conditions of [13]. The differences in the potentials calculated by the Nernst equation (11) and the mid-peak potentials of the lacunary species in Fig. 4 predict that the redox reactions proceed spontaneously. The experimental mid-peak potentials in Fig. 4 were calculated using equation (14) and the peak potentials in Fig. 3.

The proposed fuel cell operates with platinum as an electrocatalyst at the anode. The mid-peak potentials were not determined with this electrocatalyst metal because the peaks of the hydrogen reactions on a platinum electrode convolute with the peaks of heteropolyacids. Kim [13] evaluated the regeneration by fuel cell, see Fig. 1. The fuel cell testing comprises scanning the potential of the cell linearly with time and measuring the electrical current that flows through a resistor with a constant resistance. Regeneration was possible; however, the internal resistance of the fuel cell re-

sults in very low performance. One probable source of this electrical resistance is the electrostatic repulsion of the lacunary anionic species and the sulfonic ($-SO_3^-$) acid groups of the Nafion, which form part of the anode catalyst layer.

4. CONCLUSIONS

The formation of three phosphomolybdate species in each of the three pH regions determines the behavior of the pH jumps on the titration curve and produces the three signals in NMR spectroscopy. Conversely, the voltammograms show a linear variation of the redox potentials of the peaks of these species. This apparent contradiction can be explained because the metal centers in the three species are equivalent for accepting or donating electrons.

The speciation diagram indicates that H_2S has a stability region from pH 0.8 to 5.5, and the S_0/H_2S redox couple is predominant in this pH interval. Therefore, a redox reaction occurs between H_2S and the phosphomolybdate species; consequently, H_2S can donate electrons to form elemental S . The redox reaction is preceded by hydrogen-bonding interactions between the H_2S and bridging oxygen atoms of the Keggin-type structure. The number of bridging oxygen atoms and the degree of protonation/deprotonation are different in each lacunary species. Additionally, the current peaks are lower at higher pH when the predominant species has a relatively small number of bridging oxygen atoms. The results indicated that the Keggin-type structure was the most electrochemically active and consequently predicted that H_2S can be efficiently removed by this species at pH 0.8. However, the solubility of H_2S gas is lower in acidic media, and the process is strongly limited by the rate of mass transfer in a two-phase system. The experimental redox potentials of the molybdophosphate complexes obtained here and the Nernst equation of the oxygen reduction reaction permit us to conclude that the regeneration of the molybdophosphate complexes in a fuel cell is thermodynamically spontaneous. However, the phosphomolybdate species are anions and are consequently electrostatically repelled by the sulfonic acid groups of Nafion. This electrostatically repulsion severely decreases the performance of the fuel cell.

5. ACKNOWLEDGEMENTS

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