The Research on the Stability of TiO_2, MoO_3, PEO Doped Four-member Tungstic Acid Sols

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Abstract: The TiO_2, MoO_3, PEO doped four-member tungstic acid sols were prepared for the first time. The stability of different doped content sols were investigated and optimized with rotational viscometer. The four-member doped tungstic acid sol was very stable which could be stored more than two months at room temperature. The WO_3 electrochromic film prepared from this doped four- member tungstic acid sol had excellent performance and longevity of service.

Keywords: Sol, doped, four-member, stability, viscosity.

The electrochromic materials have an excellent application prospect. They are used widely on smart windows with controllable throughput of radiant energy and electronic information displays. In recent years, research on the smart window has been receiving more and more attention. By controlling the solar radiation to buildings or automobile interiors, one can modify the illumination and heat gain to improve comfort and energy conversion, taking the advantage of low power requirement. Among the electrochromic materials used in smart windows, WO_3 has attracted much attention recently due to its high coloring efficiency, low material cost and high stability. Working as the promising electrochromic material, WO_3 is usually doped with one or two efficient additives to improve its properties[1]. Certain contents of TiO_2, MoO_3, PEO can stabilize the tungstic acid sols, decrease the electrochromic potential of the prepared electrochromic film materials and prolong its cycle life[2-4]. There were a lot of reports about doped WO_3 of two or three-member electrochromic film material, but no report about doped WO_3 of four-member electrochromic film material yet.

There are several methods to prepare WO_3 film material such as electrodeposition, sputt deposition, chemical vapour deposition, electron beam deposition and sol-gel process. Recently, the sol-gel process has been proposed as a simple and new technique for preparing film material. Sol-gel technique possesses many advantages, such as low processing temperature, simple equip- ments and ready control of the film morphology[5]. The preparation of stable tungstic acid sols is the key for the preparation of WO_3 electrochromic film material of excellent performance. It was reported in this paper, the

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content select of stable MoO_3, TiO_2, PEO doped four-member tungstic acid sols samples for the first time. The stability mechanism of the sol was discussed as well.

Experimental

WO_3 and MoO_3 sols were formed upon acidification of sodium tungstate and sodium molybdate aqueous solutions passed through a proton exchange resin. TiO_2 sols were formed upon the hydrolysis of $Ti(OBu)_4$ which worked as precursor. For the preparation of TiO_2, MoO_3, PEO doped four-member WO_3 sols, with the mol ratio of $WO_3 : MoO_3 : TiO_2 = 10 : 3.3 : 0.7$ and 0.2 g PEO, $Ti(OBu)_4$ and PEO were directly dissolved in the prescribed WO_3 and MoO_3 sols. With this procedure, clear and homogeneous sols were obtained. The viscosity of different sol samples was investigated with NDJ-7 rotational viscometer in order to select the optimum content of tungstic acid sol with stable performance.

Results and Discussion

The pure tungstic acid sols were very unstable，and were changed into kelly gels within 20 minutes. The reaction could be described as follows:

$$2\,WO_4^{2-} \longrightarrow W_2O_7^{2-}$$

Such unstable tungstic acid sols could not be used to prepare WO_3 electrochromic film material. It was shown that the addition of stabilizer such as H_2O_2, $NH_3 \cdot H_2O$, CH_3CH_2OH, MoO_3, TiO_2 and CH_3COCH_3 into the tungstic acid sols could not only make the sols more stable and prolong the gelation time sharply, but also improve relevant the electrochromic performance of WO_3 film material. The viscosity curves of pure tungstic acid sol and different content of doped tungstic acid sols were shown in **Figure 1**.

It was pointed out that tungstic acid sols could be stabilized efficiently by adding MoO_3. Because W^{6+} could be partly replaced by Mo^{6+}, thus stable charged polytungstic acid sol particles with absorption of $[MoO_4]^{2-}$ ion: $[(H_2WO_4)_m \cdot nMoO_4^{2-} \cdot 2(n-x)H^+]^{2x-} \cdot 2xH^+$ were formed. But adding too much or too little MoO_3 resulted in the formation of unstable doped tungstic acids sols. The reason why TiO_2 could stabilize tungstic acid sols was still ambiguous, but the optimum ratio of $WO_3 : TiO_2$ was 10 : 0.7. Adding too much TiO_2 led to precipitation of TiO_2, while too little TiO_2 also induced the doped tungstic acids sols unstable. In addition, 0.2 g of PEO and plenty of H_2O_2 and EtOH, acetone *et al*. were also added into the doped tungstic acids sols which could be stored for more than two months at room temperature. Adding H_2O_2 into doped tungstic acids sols caused O^{2-} of $[WO_4]^{2-}$ partly replaced by O_2^{2-}:

$$[-O-O-]^{2-} + [O_3W-O]^{2-} \longrightarrow [O_3W-O_2]^{2-} + O^{2-}$$

This reaction decreased the number of O^{2-} ligands in $[WO_4]^{2-}$, and decelerated the condensation among tungstic acid and stabilized the tungstic acid sols. Other small ligand molecules such as ethanol, acetone could also coordinate with $W^{6+}$and stabilized the tungstic acid sols. The mechanism might be described as the following. For the example of ethanol :

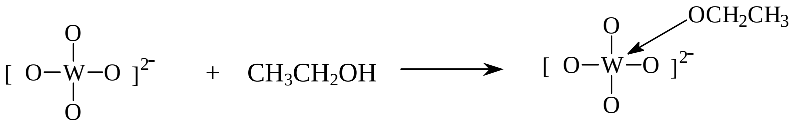
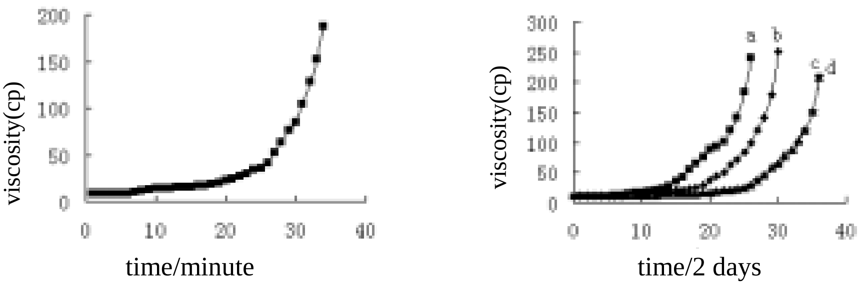


Figure 1 Stability of WO_3 sols with different content



W / T i / Mo = 10；0；0 PEO=0 g

a: W / Ti / Mo =10；0.7：0 PEO = 0.2 g
b: W / Ti / Mo =10；0 ：3..3 PEO = 0.2 g
c: W / Ti / Mo =10；0.7 ：3..3 PEO = 0 g
d: W / Ti / Mo =10；0.7 ：3..3 PEO = 0.2 g

The increase of ligands around W6+ would result in steric effect and decrease the condensation among tungstic acids, therefore the sols got more stable. But compared with H2O2, the coordinate effect of these small ligand molecules was relatively weaker. They made the sols not as stable as that of H2O2.

The gelation process of sols attributed to the rapid evaporation of solvent, elimination of H_2O and H_2O_2 from polytungstic acid sol particles resulted in the sharp augment of viscosity, and at last deposition into gels meshwork film on the substrate surface gradually. This process was not the simple repeat of condensation of tungstic acids. It was found that the preferable time for the gelation process of tungstic acid sols on the substrate surface was about 0.5-1 h. If the gelation process was too slow, the quality of formed film was poor. Therefore, there existed a contradiction on the stability of sols in the process of the preparation of film material by sol-gel method. On the one hand, we tried our outmost to prepare the sols with excellent stability performance in order to transport and manufacture easily. So it was better for the sols if it was stable enough to be stored at least several weeks even several months. On the other hand, when we prepared the film material on the substrate surface by the sols gelation, better the sols had not be so stable in order to form the high quality gels meshwork film within the preferable time of 0.5-1 h. Modulating the ratio of sols component content may solve this contradiction. It was found that much more ethanol was favorable for film formation because ethanol is more volatile than water and facilitates the rapid formation of film. While adding too much H_2O_2 into the sols, it slowed down the gelation process. The gels contracted on the substrate surface and the quality of formed film was poorer. The film quality of different content of sols was shown in **Table 1**.

Table 1 The film quality of the different content of the sols

Sample/ volume ratio	Phenomenon	Film quality
$H_2O_2 : WO_3 = 0 : 1$	rapid gelation	uniformity
$H_2O_2 : WO_3 = 1.5 : 1$	slow gelation	uneven
$EtOH : WO_3 = 2 : 1$	relatively rapid gelation	uniformity
$EtOH : WO_3 = 10 : 1$	relatively_slow gelation	uniformity

Four-member doped tungstic acids sols prepared according to content d in **Figure 1** and **Table 1** not only possessed good stability performance, but also the doped WO_3 electrochromic film material obtained from the sols had excellent performance and longevity of service.

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