

전자현미경을 이용한 산화주석 표면에 염화은의  
흡착에 관한 연구

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Electron Microscopic Study of the Adsorption of Silver  
Chloride onto Tin Oxide Thin Films

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One of the applications of a transparent semi-conducting tin oxide thin film was as an indicator electrode in potentiometric investigation of oxidation-reduction reactions<sup>1</sup>. This is the use of its inertness in a various chemical environments including strong acidic and basic

media. Also redox reaction of organic molecules as well as inorganic couples were demonstrated<sup>2</sup>. It has been pointed out that tin oxide is superior to platinum as an indicator electrode in the case of redox reactions in concentrated chloride solutions because of the formation of

$\text{PtCl}_4^{2-3}$ , and in solutions containing peroxides which decompose rapidly in the presence of platinum<sup>4</sup>.

Another application of tin oxide electrode was the possible use in the potentiometric titration of halides with silver ion<sup>1,5</sup> or *vice versa*. It gives a clear potential break to each halides. The mechanism of the sensitivity to halide ion concentration, however, has not been elaborated yet. In this communication, we report the presence and the role of adsorbed silver chloride precipitates on tin oxide, and on the potential response to the chloride ion concentration.

The specimens for the scanning

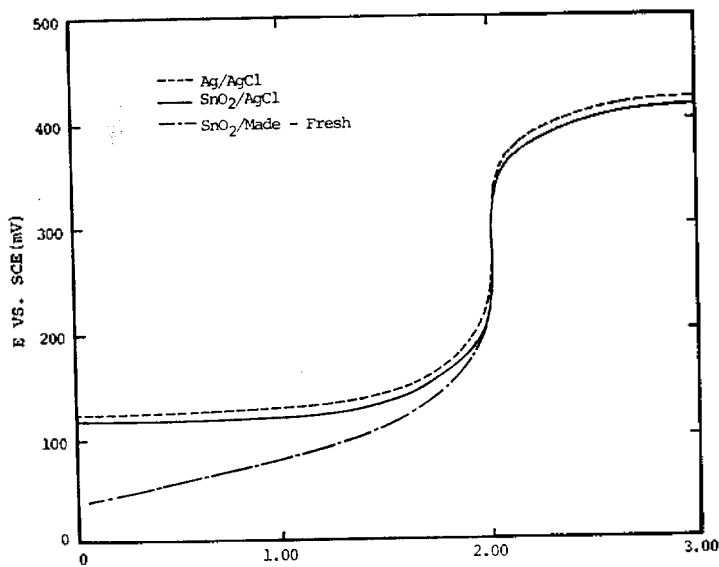
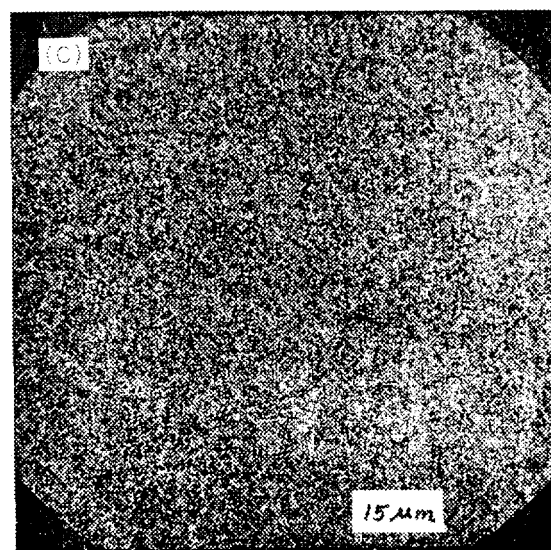
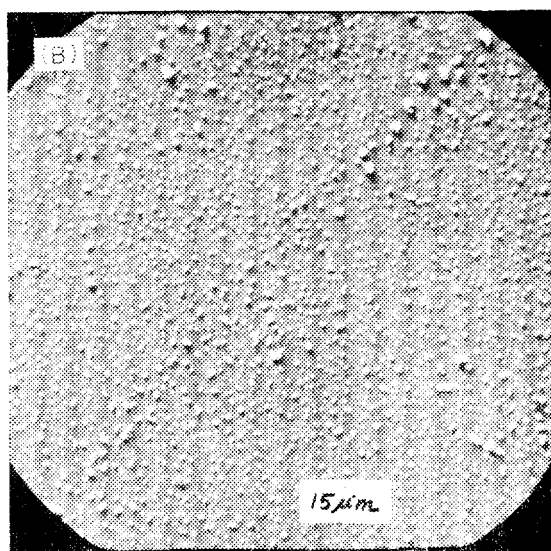
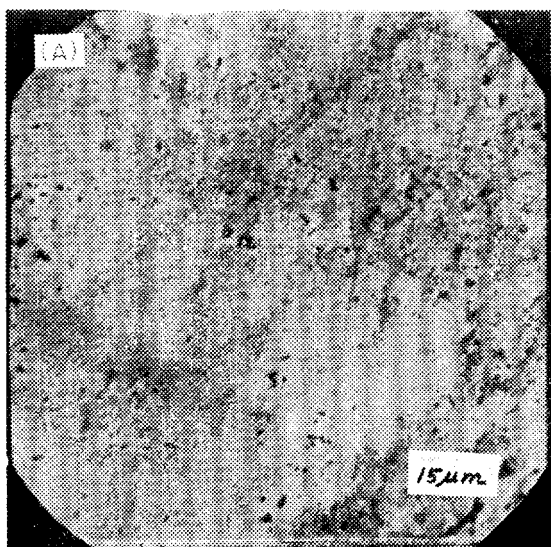


Fig. 1. Titration Curves of 20.00 ml 0.0100 M KCl with 0.100 M AgNO<sub>3</sub> solution on various electrodes.

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electron microscope were prepared by immersing tin oxide film on Pyrex substrates (2 cm × 2 cm) into 0.01 M chloride solution, then titrate with silver ion while stirring.

The tin oxide electrodes were taken out from the solution at around mid-point, and after the equivalence point in the course of titration. They were washed thoroughly with distilled water and dried in the air before mounting into electron microscope. Potentiometric potential measurements were made on tin oxide electrode with a metal clip for electrical contact against a standard saturated calomel reference electrode. Tin oxide films were made on Pyrex glass plates by spraying acidic stannic chloride with 2 mole percent antimony as dopants<sup>12</sup>.

General titration curves on fresh tin oxide and on AgCl adsorbed tin oxide as well as on Ag/AgCl are shown in Fig. 1. It always showed that the freshly made tin oxide electrodes or ones polished the surface with alumina after exposure to AgCl did not respond to a theoretical titration curve in the beginning. But those used in titration once, they gave a Nernstian behavior to different chloride ion concentration. It was also noticed that the silver chloride precipitates were on the surface after being exposed to the solution containing AgCl. On the little potential difference between Ag/AgCl and SnO<sub>2</sub>/AgCl electrodes will be discussed in the later paper.

The scanning electron microscopic pictures are in Fig. 2. In the Fig. 2-A, it shows a clean tin oxide surface while 2-B and 2-C show the surface are covered with AgCl precipitates. They were the specimens taken out of solution before and after the equivalence point in the

Fig. 2. Scanning electron microscope pictures. A : Fresh tin oxide surface. B : Tin oxide with a partial coverage of AgCl. C : Tin oxide with a complete coverage of AgCl.

titration, respectively. We could see that the surface was completely covered with AgCl, especially ones have taken out after the equivalence point. The adsorbed precipitates were positively identified by the use of X-ray element analyzer for silver and chloride. Also they gave a perfect Nernstian slope in the potential measurement. This complete coverage of the surface with AgCl was observed from solutions with pH value between 4 and 10.5, outside which the potential was related to proton ion and hydroxyl ion concentration as well.

All of the solid state halide ion selective electrodes have silver halides in various matrix forms, such as in cast pellets<sup>6,7</sup>, in polymerized silicone rubber<sup>8</sup>, in thermoplastic polymer<sup>9</sup>, and in pellets of gold powder<sup>10</sup> and silver powder<sup>11</sup>. Therefore, when the tin oxide surface has been covered by AgCl precipitates, should work as a chloride ion selective electrode.

The remaining of chloride in tin oxide lattice<sup>12</sup> makes it easy for silver ion or silver chloride to be adsorbed onto the surface. This is the main difference between platinum and tin oxide. When a platinum electrode was exposed to AgCl, it was not possible to have all surface covered. So it gave a far less than 60 mV/decade Nernstian slope. In the case of a fully AgCl-coated gold ball, the Nernstian behavior was observed<sup>10</sup>.

In conclusion, when tin oxide material was exposed to silver chloride precipitates, the surface was covered with silver chloride and established a boundary potential which was related

to the concentration of chloride or silver ion by Nernstian fashion.

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