Effect of Water Impurity on Insulating Property of Niobium Anodic Oxide Film in Organic Electrolyte.

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Introduction

Tantalum solid electrolyte capacitor is in practical use due to its excellent features such as a small mass and large capacitance. Since the resources of tantalum are rare, they are expensive and price fluctuates by the unstable supply. Recently, many attentions have been made for niobium as an alternative anode material. The relative dielectric constant of a niobium anodic oxide film is about 40, and this enables us for high capacitance. However, the leakage current of niobium anodic oxide film is higher than that for tantalum, and this is strongly affected by the heat treatment in the fabrication process and the bias potential. To overcome this problem, many researches have done, but they were focused on the oxide film | electrolyte solution interface. In this research, we focused on the effect of the water impurity in organic electrolyte on the leakage current at an oxide film | solid electrolyte interface of which was similar to an actual solid electrolyte capacitor.

Experimental

The working electrode was fabricated by rolling the part of 13cm niobium wire (0.3mm in dia., 99.9%, NILAKO) to spiral shape for about 7 mm in diameter with remaining 3 cm as a lead wire. This electrode was pretreated by alkaline degreasing, then the anodic oxide film was made by constant current oxidation by 1 mA/cm^2 in 0.1M phosphoric acid solution. After the potential reached to 20V (vs. Ag/AgCl), 20 minutes aging process was carried out under the constant potential at 20V.

Manganese dioxide (IC-21, ITE) was heat-treated at 400℃ for 6 hours, and used as a solid electrolyte of which was contacted on a niobium anodic oxide film. 50mg of manganese dioxide and three drops of TEFLON dispersion were well kneaded, and pressed on to the electrode by 1 kgf/cm^2, then vacuum dried at 120℃ centigrade for 6 hours. The leakage current was measured by the chronopotentiometry. 1M LiBF$_4$ in PC+ DME (50:50) with some water impurity was used as an electrolyte. The Pt counter electrode and Ag quasi-reference electrode was used. Water content was measured by Karl-Fischer method.

Results and discussion

Fig.1 shows the chronopotentiograms of the niobium and tantalum anodic oxide formation and the following chronoamperograms for the aging process. Potential increasing rate for tantalum was higher than that for niobium, indicating that the leakage current of niobium anodic oxide film was larger than that of tantalum anodic oxide film.

Thus formed niobium anodic oxide film was contacted with MnO$_2$ solid electrolyte and soaked in organic

electrolyte, then the chronopotentiograms were measured as a function of water content as shown in Fig.2. When the constant current was applied, very steep potential increase were observed, and soon reached their break potential of the anodic oxide film to appear as the potential peak in chronopotentiometry. The potential at which the 400 seconds passed under controlled constant current of 1 mA/cm^2 is shown in a table 1. It was clear that the potential increased with increasing water content. This was a clear indication that the water was an excellent repairing material of the defective part (i.e. point defects) of the niobium anodic oxide film, and thus the leakage current was decreased by the water impurity.
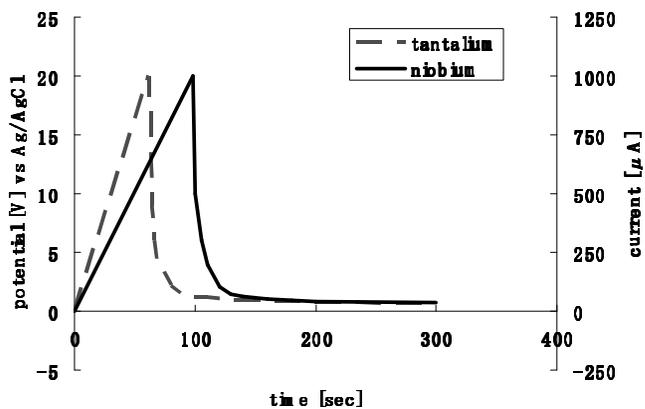

Fig.1 Chronopotentiograms and the following chronoamperograms of tantalum and niobium anodic oxide formation process in 0.1M phosphoric acid solution.
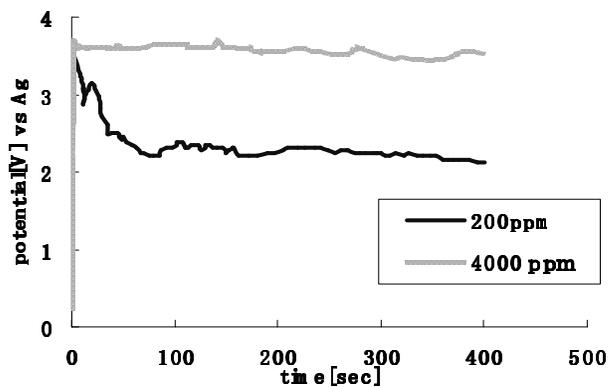

Fig.2 Chronopotentiograms of niobium anodic oxide film | MnO$_2$ solid electrolyte interface as a function of water content in organic electrolyte solution.

Table.1 The potential of niobium anodic oxide film | MnO$_2$ solid electrolyte interface at which the 400 seconds passed under controlled constant current of 1 mA/cm^2 as a function of water content in organic electrolyte.

Water Content	E (vs. Ag) after 400s
200 ppm	2.06 V
4000 ppm	3.57 V

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