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Creation of Functional Materials by Electric Field in Solution

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Movement and deposition of particles according to an electric field in solution can be applied to a creation of functional materials and devices. This deposition method is so-called "Electrophoretic Deposition (EPD)". In this study, electrodes in rechargeable lithium batteries, ceramic filters, and coating of photocatalytic particles on substrates, were introduced in order to demonstrate a usefulness of the EPD process for fabrication of ceramics.
Key words: electrophoretic deposition, rechargeable lithium batteries, ceramic filter, TiO_2, Al_2O_3, graphite

1. INTRODUCTION

Various fabrication methods have been utilized to many kinds of devices. [1-27] An electrophoretic deposition process is one of promising techniques to fabricate powder samples. In fact, this method has been utilized to prepare thin film of various ceramics. Most of particles in solutions have a surface charge depending on conditions of solutions. Therefore, more or less, such particles can move according to an electric field, when a relatively high voltage is applied between two electrodes. Finally, particles touch to electrode and simultaneously discharge to keep an electrical neutral condition. This process continues to make an accumulation of particles on an electrode. A deposition of particles through these processes is so-called "Electrophoretic Deposition Process (EPD)". The schematic illustration of EPD process is shown in Figure 1. An electric field is used as an external force for a fabrication of particles.

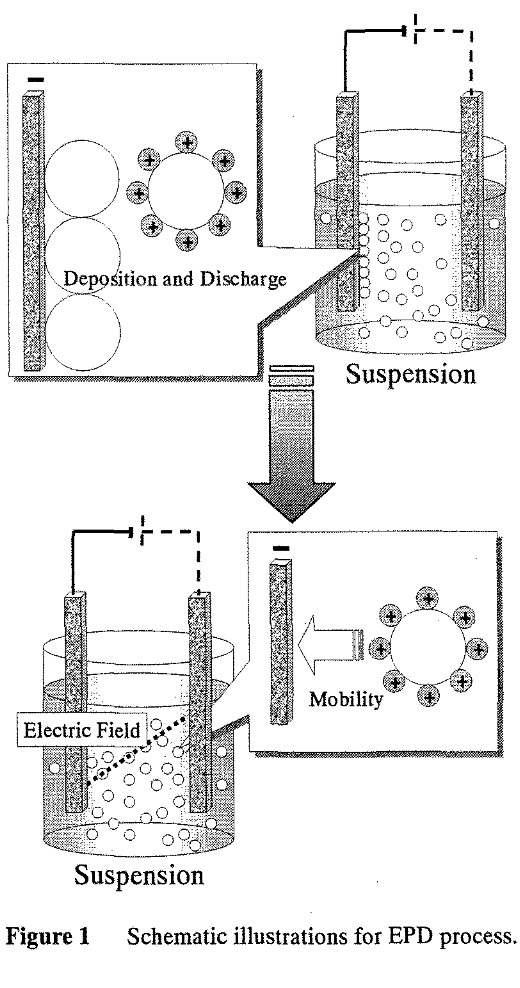

Figure 1 Schematic illustrations for EPD process.

2. EXPERIMENTAL

The electrophoretic deposition of several kinds of transition metal oxides and carbon materials were performed using a simple glass cell as shown in Figure 1. In this study, four different metal oxides were used as particles for the electrophoretic deposition. $LiCoO_2$ and $LiMn_2O_4$ are used as cathode materials for rechargeable lithium batteries. [21, 22] TiO_2 (Aerosil Japan Ltd., Titanium dioxide P25) is selected as photocatalysts. [25] Al_2O_3 is chosen as materials for ceramic filter. [26, 27] Moreover, graphite particle is used as carbon material having a strong particle orientation, which has been utilized to anode material for rechargeable lithium batteries. Experimental details were described below.

2.1 Electrodes for Rechargeable Lithium Batteries [21, 22]

Electrodes (positive and negative electrodes) for rechargeable lithium batteries consist of active material ($LiCoO_2$, $LiMn_2O_4$, graphite, and so on), polymer binder (Poly-Vinylidene Fluoride (PVdF), Poly-Tetrafluoro Ethylene (PTFE)), and carbon black (ketjene or acetylene black) with a proper weight ratio. In this study, suspensions involving these materials were prepared for an electrophoretic deposition process of each active material. Acetone solution with a small amount of I_2 was used as a solvent to prepare the stable suspension. [23, 24] Amounts of three components in the suspensions were optimized to obtain a proper weight ratio.

2.2 Photocatalyst Layer [25]

TiO_2 fine particles have been deposited on a substrate for various applications. As well known, TiO_2 particles have a high photocatalytic activity, which is very useful to decompose organic compounds by photochemical reactions. However, its photochemical activity depends on a physical state of coated TiO_2 fine

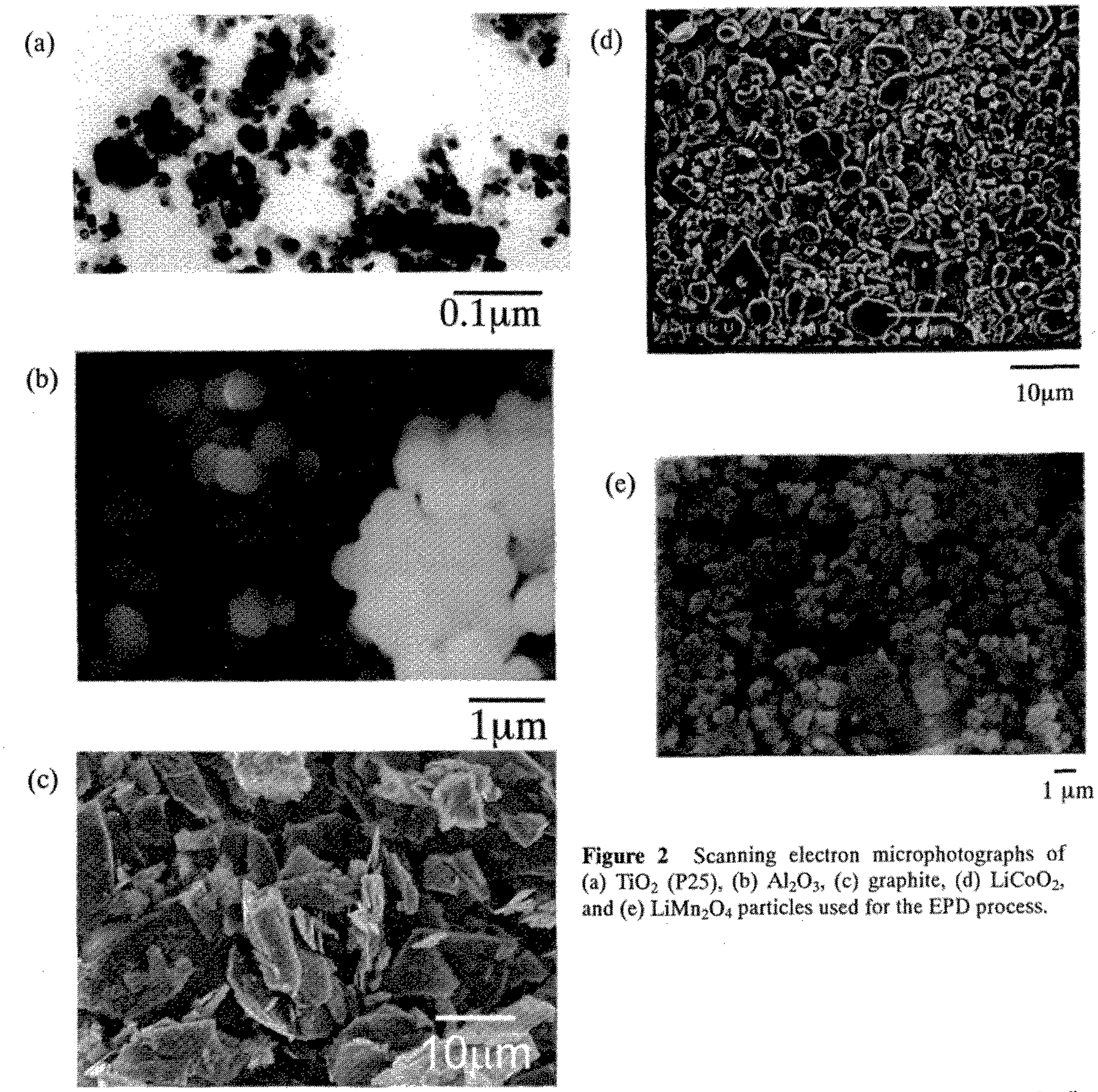

Figure 2 Scanning electron microphotographs of (a) TiO_2 (P25), (b) Al_2O_3, (c) graphite, (d) $LiCoO_2$, and (e) $LiMn_2O_4$ particles used for the EPD process.

particle, so that the coating process of TiO_2 fine particles is very important. In this study, TiO_2 fine particles with polymer, such as Teflon or Nafion, was conducted to obtain a stable thin layer of TiO_2 fine particles. A suspension for this electrophoretic deposition was prepared by mixing of TiO_2 (P25) fine particles and polymer dispersed in H_2O, ethanol, or acetone. A weight ratio between TiO_2 particles and polymer was optimized to obtain a high photochemical activity and a high stability of coated film.

2.3 Ceramic Filter [26, 27]

Ceramic filters have been used to eliminate inorganic particles, collides, organic particles, and virus from wasted water. For this purpose, a pore size of the ceramic filter must be controlled. In this study, porous Al_2O_3 tube was used as a substrate and its pores was filled with fine particle of Al_2O_3 powder. The coating of fine Al_2O_3 powder should be done uniformly, otherwise some of smaller particles, especially virus, go through the ceramic filter. In order to uniform deposition, in this study, an electrophoretic deposition was utilized. Al_2O_3 aqueous suspension (1 g / 50 mL H_2O) was used for the electrophoretic deposition. The diameter of Al_2O_3 fine particles was 0.78 μm.

Figure 2 shows scanning electron micrographs for particles used in this study. The shape of $LiCoO_2$, $LiMn_2O_4$, TiO_2, and Al_2O_3 particles were not so anisotropic. On the other hand, graphite had a highly anisotropic shape.

3. Results and Discussion

3.1 Electrodes for Rechargeable Lithium Batteries

Electrodes in rechargeable lithium batteries work as an insertion electrode. Therefore, both electric and ionic path have to be involved in both negative and positive electrodes. In order to prepare such an electrode, a uniform particle distribution and a good contact are needed. In this study, the EPD was applied to a fabrication of such kind of electrode.

Figure 3 shows scanning electron micrographs for $LiCoO_2$ and $LiMn_2O_4$ electrodes prepared by the EPD under the optimized conditions, as shown in Table 1. Amounts of binding polymer and acetylene black

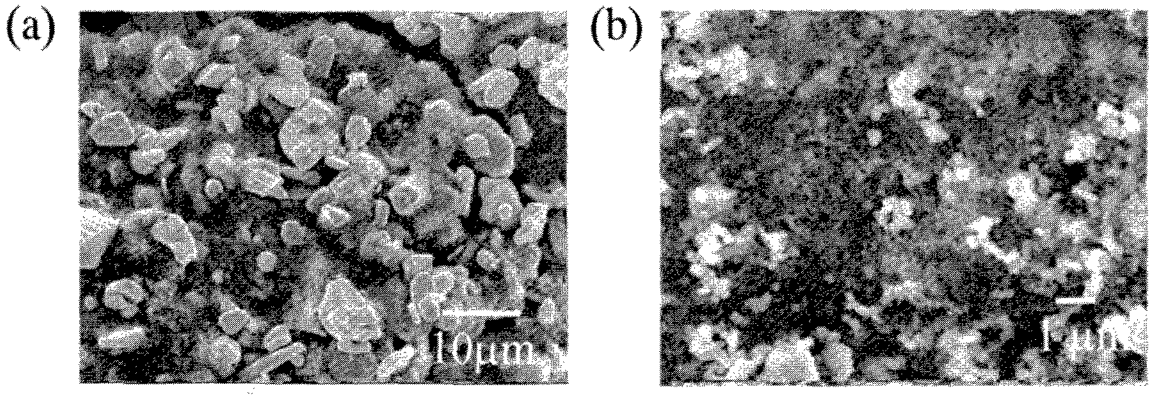

Figure 3 Scanning electron micrographs of (a) $LiCoO_2$ and (b) $LiMn_2O_4$ electrodes prepared by the EPD process under optimized conditions.

Table 1 Optimized conditions of suspension and EPD process.

	Active Material	Ketjen black	PTFE binder	I_2	Voltage
$LiCoO_2$	500 mg / 50 mL acetone	10 mg / 50 mL acetone	24 mg / 50 mL acetone	5 mg / 50 mL acetone	400 V / cm
$LiMn_2O_4$	500 mg / 50 mL acetone	5 mg / 50 mL acetone	24 mg / 50 mL acetone	10 mg / 50 mL acetone	400 V / cm

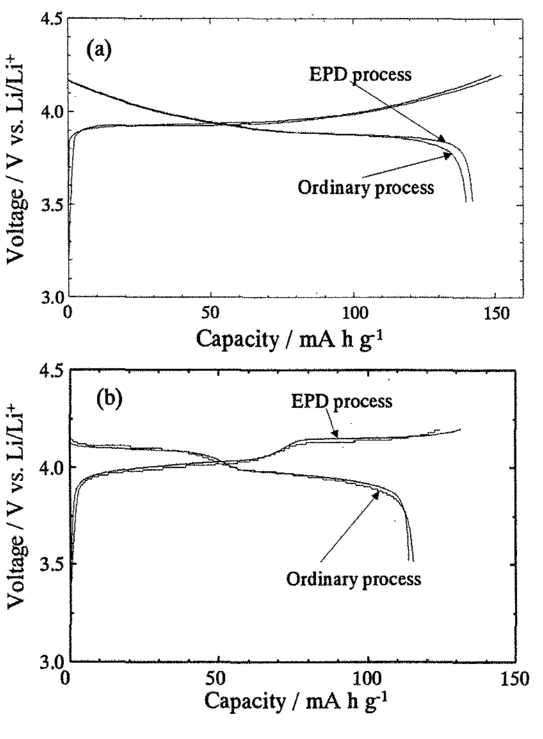

Figure 4 Discharge and charge curves of (a) $LiCoO_2$ and (b) $LiMn_2O_4$ electrodes in 1M $LiClO_4$/ethylene carbonate + diethyl carbonate, discharge and charge cut off potential: 3.5 V and 4.2 V, discharge and charge rate: 0.1 C.

depended on dispersed their amounts on acetone solution. Accordingly, the electrochemical performances of these electrodes were changed with suspension conditions. In these EPD processes, each component did not deposited, independently. Probably, three components, active material, Ketjene black, and PTFE, interact each other in the suspension solution to form precursor particles. Therefore, the preparation of the suspension is very important. Figure 4 shows the discharge and charge curves of the prepared $LiCoO_2$ and $LiMn_2O_4$ electrodes. In this figure, the discharge and charge curves of $LiCoO_2$ and $LiMn_2O_4$ prepared by an ordinary process were also shown to compare with those prepared by the EPD processes. The $LiCoO_2$ prepared by the EPD showed an identical electrochemical behavior with an ordinary electrode. This means that the EPD process is very useful for the $LiCoO_2$ electrode preparation. On the other hand, the $LiMn_2O_4$ prepared by the EPD showed a relatively lower discharge capacity. This may be caused by a lower electric and/or ionic conductivity of the prepared electrodes. The particle size of $LiCoO_2$ (5-10 μm) was larger than that of $LiMn_2O_4$ (less than 1 μm). In general, a smaller particle results in a larger contact resistance between particles and lower porosity of electrode. Therefore, a larger $LiMn_2O_4$ particle should be used in the EPD process.

Figure 5 shows scanning electron micrographs of graphite electrode prepared by an ordinary and EPD processes. The graphite particle has a high anisotropy of particles. Especially, an electrochemical reaction of graphite electrode is explained by Li^+ ion intercalation and deintercalation. These reactions take place on an edge plane of graphite particles, as shown in Figure 6. Therefore, the orientation of particles deposited on substrates is very important. When an ordinary process is used for the fabrication process, the orientation of graphite is not good for battery use. In the case of the EPD process, such undesirable orientation of graphite is improved because of an electric field and resistance of solvent for movement of graphite particles. This is confirmed by the results in Figure 5. The orientation of graphite particles prepared by the EPD is slightly

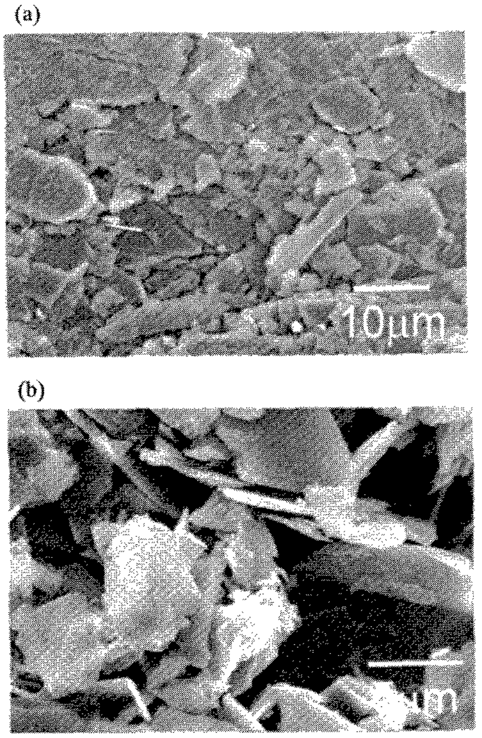

Figure 5 Scanning electron micrographs of graphite electrodes prepared by (a) ordinary process and (b) the EPD process.

improved. However, the density of the prepared electrode was too low to realize a good electric contact between graphite particles in the prepared electrode. In fact, the discharge and charge characteristics of the prepared graphite electrode were not good as that of an ordinary electrode. Therefore, denser electrode should be prepared.

3.2 TiO_2 Photocatalyst with Polymer

A photocatalytic activity of TiO_2 depends on its surface area and crystallinity. Moreover, when TiO_2 (P25) is used in a form of a thin film, the surface state of the film is a key factor. The EPD process is one of easy fabrication processes for fine ceramic powder thin film without any heat treatment. In the case of TiO_2, if heat treatment at a few hundreds °C were performed to prepare the thin film, the catalytic activity of TiO_2 would be decreased due to a growth of crystal. Therefore, the EPD process may be suitable for a fabrication of TiO_2 thin film. However, mechanical stability of the TiO_2 thin film without a heat treatment is not so strong. In this study, TiO_2 and PTFE or Nafion® polymer were simultaneously coated on a substrate in order to improve a mechanical adhesion. Figure 6 (a) shows a scanning electron micrograph of the TiO_2 thin film prepared by the EPD process. There were many serious cracks in the obtained thin film. Figure 6 (b) shows a scanning electron micrograph of the prepared TiO_2 thin film with Nafion® polymer. In this case, there were still cracks in the TiO_2 thin film. However, serious cracks were significantly decreased. Figure 6 (c) shows a scanning electron micrograph of the TiO_2 thin film with PTFE.

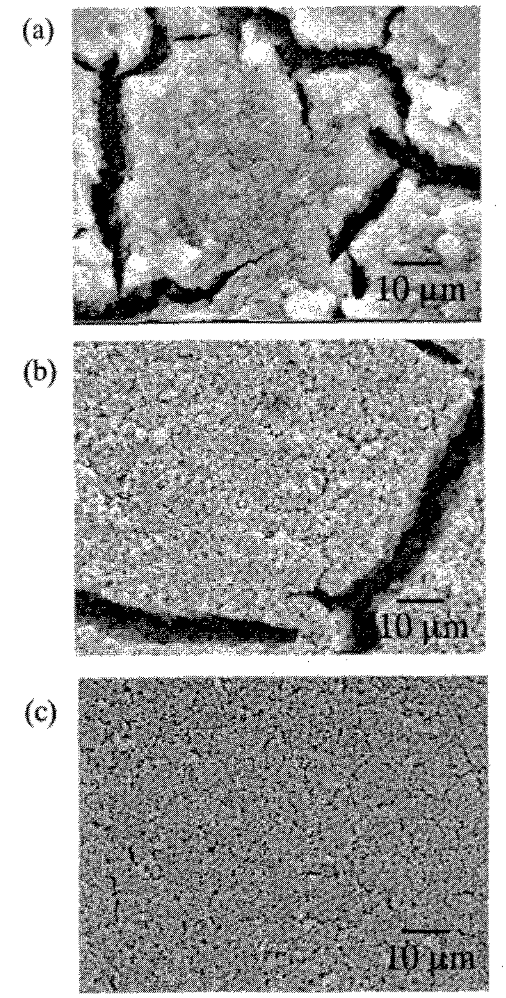

Figure 6 Scanning electron micrographs of TiO_2 film (a) without polymer, (b) with Nafion®, and (c) with PTFE.

There were almost no cracks in the film. Thus, a polymer binder can control the physical state of the prepared thin film and also a mechanical strength of the thin film. The most smooth surface morphology was obtained when 0.2 mL PTFE and 1 g TiO_2 was put into 50 mL suspension (acetone). The photocatalytic activity of the thin film was examined by a decomposition of methylene blue (MB) through an irradiation of ultra-violet light. Figure 7 shows a decomposition rate of MB. An original TiO_2 (P25) powder showed a high decomposition rate. The thin film of TiO_2 with PTFE showed a lower activity. This may be due to a low interaction between aqueous solution and the TiO_2-PTFE composite film. Probably, this type of the film is good for decomposing organic compounds in a gas phase.

3.3 Ceramics Filter (water purification)

In all above examples, materials were deposited on a substrate with an electronic conductivity. In this case, the substrate was nonconductive ceramic, but it was porous. Figure 8 shows the schematic illustration of the cell for tubular type EPD. The tubular substrate was Al_2O_3 and very porous. A rod Pt electrode was put into

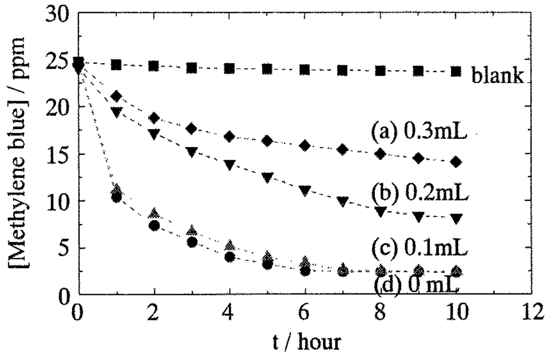

Figure 7 Decomposition of MB at room temperature under irradiation of black light (15 W).

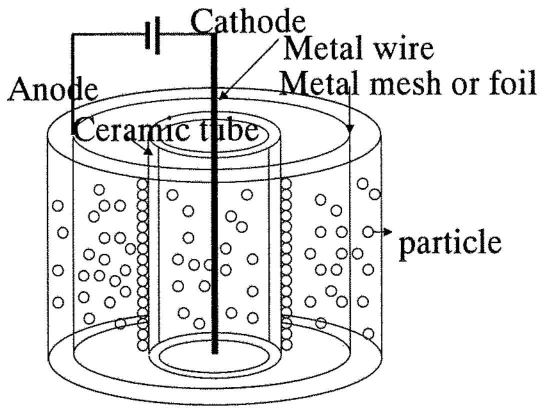

Figure 8 Schematic illustration of EPD cell for porous tubular substrate.

the center of the tubular substrate and the large mesh Pt electrode was set outside of the substrate. The electric field was produced between two electrodes through pores in the Al_2O_3 substrate. According to this electric field Al_2O_3 fine powders suspended in water were moved from - electrode to + electrode. Most of Al_2O_3 powder did not go through pores in the Al_2O_3 substrate. Therefore, accumulations of Al_2O_3 fine powders at the outside of the Al_2O_3 substrate. Figure 9 shows a scanning electron micrograph of a cross-section of the Al_2O_3 substrate with an Al_2O_3 fine powder layer. From this photograph, it can be seen that the Al_2O_3 substrate consists of large particles and the outer layer prepared by the EPD consists of fine Al_2O_3 particle layer. After the EPD, the average pore size was changed from 0.75 μm to 0.14 μm. A heat treatment was performed after the EPD to improve a mechanical strength of the outer layer. Since pressurized water goes through this filter, the high mechanical strength of the outer layer is necessary. Figure 10 shows a performance of the prepared ceramic filter. All of bacteria were removed by a filtration using the prepared Al_2O_3 tube.

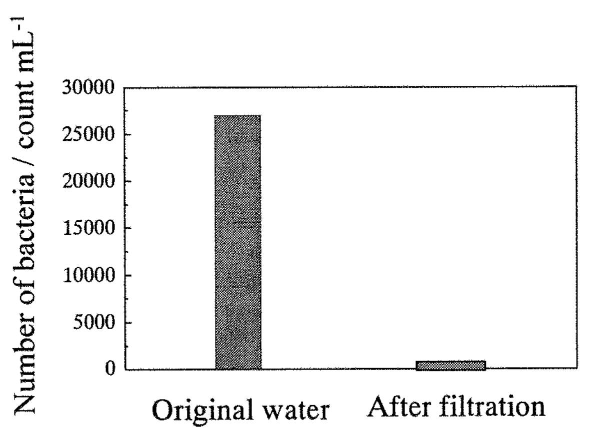

Figure 10 Number of virus in water before and after filtration using Al_2O_3 ceramic filter prepared by EPD process.

4. CONCLUSION

As shown above, the EPD is very useful to prepare thin film on some substrates without an instrumental difficulty and long preparation time. In other words, an

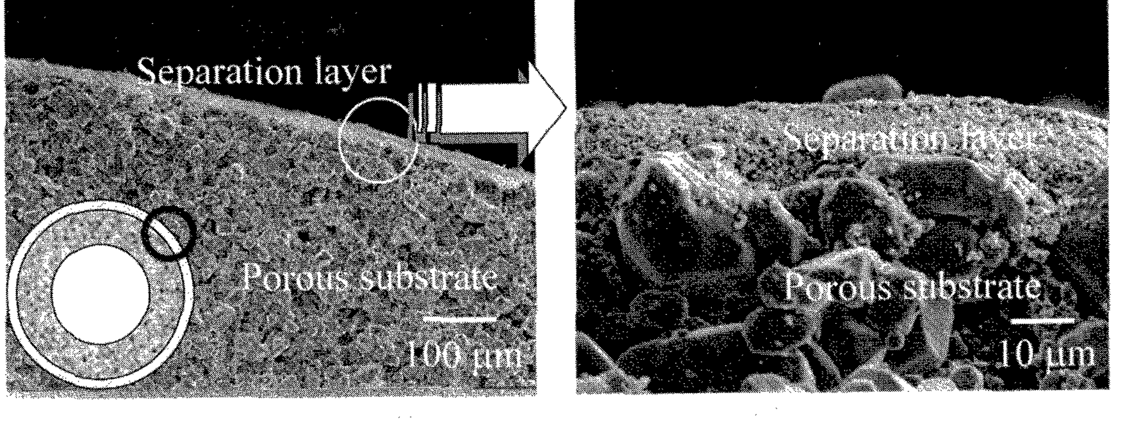

Figure 9 Scanning electron micrographs of Al_2O_3 porous substrate after EPD of Al_2O_3 fine particle, (a) porous substrate and (b) fine particle layer.

electric field is one of useful external force for a fabrication of material. In this study, the electric field was used only for a fabrication of thin film. However, if the electric force is precisely controlled, various kinds of ceramic agglomerates in a micro-scale.

5. REFERENCES

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