Bubble-free electrophoretic deposition of aqueous zirconia suspensions with hydroquinone

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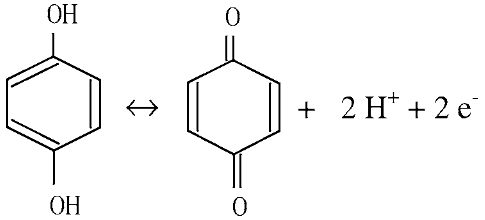
Electrophoretic deposition (EPD) is a colloidal processing technique for ceramics in which charged particles move toward, and are deposited upon an electrode with the opposite charge [1–3]. The EPD technique has many advantages, such as the fast, easy, and uniform formation of complex shapes, good control of deposition thickness, high green density. This method has been used to fabricate thin films, multilayered composites, functional materials, etc. Non-aqueous suspensions are usually preferred for the EPD process to prevent electrolysis of the solvent and to obtain bubble-free deposition. On the other hand, an aqueous shaping system is advantageous from the viewpoints of ecology, safety, and cost. Water is decomposed into hydrogen and oxygen when a DC current is passed through an aqueous medium. There have been some reports of the fabrication of a bubble-free deposit from aqueous suspension [4, 5]. Recently, Uchikoshi *et al.*, investigated the EPD characteristics of positively charged particles onto various cathodic substrates using aqueous alumina suspensions [5]. They found that no macro pores were formed in the EPD deposit on a palladium cathode, and that the green density and sintered properties of the deposits were the same as those produced by the slip casting process.

It is well known that hydroquinone (HQ) is readily oxidized to quinone (Q) at high pH in alkaline solution [6]:



In addition, the complementary reaction is reduction of the dissolved or oxygen produced electrolytically:

$$4H^+ + 4e^- + O_2 \leftrightarrow 2H_2O$$

We hypothesized that the oxygen produced electrolytically by the EPD process at basic pH would be consumed by chemical oxidation of HQ and that a bubble-free deposit would be produced on an anodic substrate. In this study, we investigated the EPD characteristics of negatively charged zirconia particles onto palladium or SUS anodic substrates using an aqueous zirconia suspension with various concentrations of HQ at basic pH.

A commercial zirconia powder doped with 3-mol%-yttria (TZ-3YS, Tosoh Co. Ltd., Tokyo, Japan) was used and 2 vol% zirconia aqueous suspensions were prepared by ball milling for 24 h to break the agglomerates. The BET specific surface area and crystal size of the zirconia were 6.8 m^2/g and 38 nm, respectively. Tetramethylammonium hydroxide aqueous solution (Aldrich Chemical Co., Inc., Madison, WI) was used for pH adjustment. Hydroquinone (HQ) (Nacalai Tesque Inc., Kyoto, Japan) was added to the suspensions to obtain bubble-free deposits. The acidity of suspensions was determined with a pH/ion/conductivity meter (Model Accumet 50, Fisher Scientific Co., Pittsburgh, PA) using a glass combination electrode (Model 8172 ROSS Sure-Flow® pH Electrode, Orion Research, Inc., Beverly, MA). The dynamic mobility versus pH of the alumina suspension was measured using an acoustic spectrometer (Model DT-1200, Dispersion Technology, Inc., Mt. Kisco, NY) to determine the particle surface charge. The water used to prepare all of the sample solutions was distilled and purified with a Milli-Q system (Milli-Q Plus, Millipore Corporation, Billerica, MA).

Well-dispersed suspensions with low viscosity were used for EPD. Deposition was performed using a DC power supply (Model PS-1510, Toyo Seisaku-sho Co. Ltd., Chiba, Japan) operating at a constant current of 1.0 mA/cm^2. Palladium sheets or stainless steel sheets with a deposition area of 2 cm^2 were used as the anode and cathode. They faced each other at a distance of 2 cm. The obtained deposits were dried in air at room temperature and weighed together with the anodic substrates to determine the weight of deposited material.

Suspension stability can usually be obtained by pH adjustment. Repulsive forces result from the zeta potential in the particles, which protects fine particles from agglomeration and leads to a higher packing density in the sediment. The uniform and denser green parts generally show good sintering behavior and mechanical properties. The charge on a hydrated surface of a pure oxide particle dispersed in water is determined by its reaction with H^+ or OH^- ions. The addition of H^+ ions will reduce the pH and cause the uncharged

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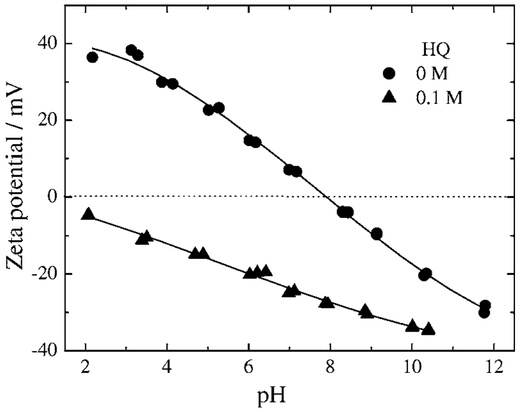

Figure 1 The electrokinetic behavior of aqueous zirconia suspensions with or without HQ as a function of pH.

surface to become protonated and positively charged. The addition of OH^- ions will remove hydrogen from the surface and produce a negative surface charge when the pH is greater than the isoelectric point (IEP) [7, 8]. Fig. 1 shows the electrokinetic behavior of aqueous zirconia suspensions with or without HQ as a function of pH. The zeta potential is strongly dependent on the suspension pH. The zirconia particles have an IEP at around pH 8 without HQ. As the pH value decreased from 8 to 3, the value of the zeta potential increased. This was attributed to adsorption of the H^+ ions onto the particle surfaces, which enhanced the electrostatic repulsion force. However, with the addition of more H^+ ions to the suspension, i.e., when the pH value decreased from 3 to 2, the large number of positive ions resulted in a reduction of the double layer thickness and, hence, a reduction of the repulsive force between the particles. A similar phenomenon was observed at alkaline pH, but with the adsorption of negative OH^- ions in the suspension. Raising the pH from 8 increased the zeta potential negatively for the zirconia particles and the system became more stable. However, at alkaline pH, the measured zeta potential appeared to be much lower in absolute magnitude than that at acidic pH. On the other hand, in the presence of 0.1 M HQ the absolute zeta potentials of zirconia suspensions increased with increasing pH and there was no IEP over the pH range examined. Polymeric products can be formed in alkaline solution in the presence of aerial oxygen [6, 9]. In a preliminary experiment, we tested the precipitation reactions of HQ aqueous solution with anionic dyes, such as methyl orange and fluorescein, and the cationic dye toluidine blue in solution at pH 10. Table I shows the results of these experiments, together with the results obtained with poly(diallyl dimethyl ammonium chloride) (PDADMC) as a polycation, potassium poly(vinyl sulfate) (KPVS) as a polyanion, and NaCl as a typical electrolyte. HQ and KPVS react to form precipitates with cationic dyes; however, they do not react with anionic dyes. PDADMC, as a polycation, reacts to form precipitates with anionic dyes. NaCl, which dissociates and forms simple hydrate ions in aqueous solution, does not react with anionic or cationic dyes. As a result, the HQ-Q system yielded negatively charged and polymeric or cluster species in aqueous solutions. Therefore, the zeta potential of zirconia suspension with HQ showed negatively charged surfaces over the pH range examined. Unfortunately, we could not determine their conformation or size from the results of this experiment.

TABLE I Precipitation reaction with several dyes

	Anionic dyes		Cationic dye
	Methyl orange	Fluorescein	Toluidine blue
HQ	−	−	+
KPVS	−	−	+
PDADMAC	+	+	−
NaCl	−	−	−

PDADMAC: poly(diallyl dimethyl ammonium chloride) as polycation; KPVS: potassium poly(vinyl sulfate) as polyanion.
+ indicates precipitation.

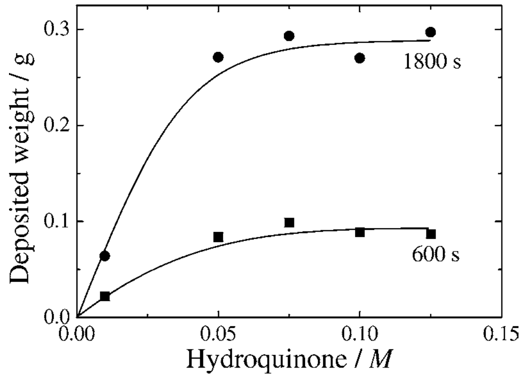

Figure 2 Deposition weight as a function of HQ concentration and deposition time. The suspension was initially prepared at pH 12.

Fig. 2 shows the deposition weight as a function of HQ concentration at different deposition times. The suspension that was used for deposition was initially prepared at pH 12. Due to the generation of bubbles on the electrode, no deposition was observed without HQ. Independent of the deposition time, the weight of deposited material increased with increasing HQ concentration up to 0.05 M HQ and then showed a constant value. The voltage versus deposition time curve is shown in Fig. 3. This figure shows the voltage measured between the electrodes during constant current deposition. At HQ < 0.01 M, the voltage was over 2.5 V immediately after EPD. In addition, no deposition was observed because of the large number of bubbles generated on the electrode. At HQ > 0.05 M, the voltage

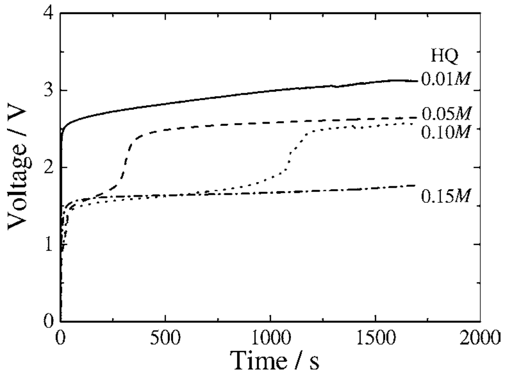

Figure 3 Voltage measured between the electrodes during constant current deposition. The suspension was initially prepared at pH 12.

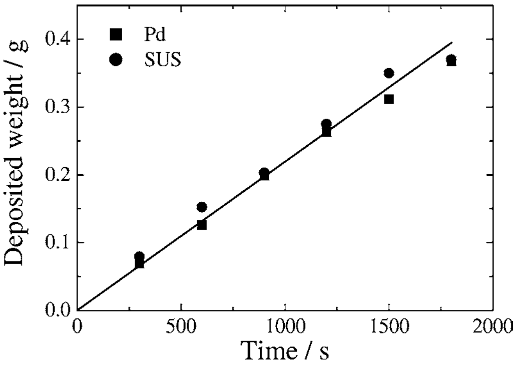

Figure 4 Deposition weight as a function of deposition time on Pd or SUS anodic electrodes.

was initially 1.6 V. The voltage of 1.6 V was maintained for longer with increasing HQ concentration; i.e., 200, 750, and 2000 s at 0.05, 0.1, and 0.15 M HQ, respectively. No bubbles were observed on the electrode, and bubble-free deposition was obtained until 310, 1100, and 2000 s at 0.05, 0.1, and 0.15 M HQ, respectively. The voltage jump from 1.6 to 2.5 V was accompanied by the decomposition of HQ.

Fig. 4 shows the deposition weight as a function of deposition time onto palladium or SUS anodic substrates. In this system, the deposition weight was proportional to the deposition time and there was no difference between palladium and SUS anodic substrates.

Bubble-free zirconia layers were readily prepared from basic zirconia suspensions by electrophoretic deposition in the presence of HQ. These observations indicate that HQ is an effective additive for the EPD. Either palladium or SUS could be used as the anodic substrate.

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