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# Experimental verification of pH localization mechanism of particle consolidation at the electrode/solution interface and its application to pulsed DC electrophoretic deposition (EPD)

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## Abstract

Experimental measurement and verification of the pH localization at the electrode/solution interface was conducted during continuous and pulsed DC electrophoretic deposition (EPD) from aqueous solution. Application of pulsed DC enabled controlling bubble incorporation and obtaining bubble-free deposits during electrophoretic deposition (EPD) from aqueous suspension. The pH localization at the electrode/solution interface on application of electric field was attributed as the underlying mechanism of particle consolidation during continuous as well as pulsed EPD. The suspension pH tends to shift towards isoelectric point (i.e.p.) leading to spontaneous coagulation of particles at the electrode. Application of continuous DC tends to attain the i.e.p. faster and closer compared to pulse DC leading to maximum deposit yield. The kinetics and closeness of attainment of pH towards i.e.p. decreased progressively with decreasing pulse size resulting in a corresponding decrease in deposit yield.

*Keywords:* Electrophoretic deposition; Pulse DC; Aqueous suspension; Electrolysis; pH localization

## 1. Introduction

Electrophoretic deposition (EPD), a colloidal forming process has now gained widespread application starting from traditional ceramics as well as wide range of advanced materials and coatings to nanotechnology because of its simplicity, low cost and versatility of coating on flat as well as curved surface. It has been used to fabricate thin as well as thick films, laminates, functionally graded materials, hybrid materials, micropatterned colloidal assemblies, etc.[1–3] In electrophoretic deposition, the powder particles dispersed in the liquid medium are attracted and migrate towards the electrode of opposite polarity on which they eventually get deposited. In general, organic liquids are used as the suspending medium in EPD because the use of water results in electrolysis of water and evolution of hydrogen and oxygen gases at the electrodes on application of electric field. Incorporation of these gas bubbles in the deposit leads to low deposit quality. But since the organic liquids are hazardous, expensive and not environmental friendly, many research groups have shown great interest to develop aqueous EPD. Very recently, we have developed a novel method based on application of pulsed DC instead of continuous DC to suppress and eliminate bubble incorporation during aqueous electrophoretic deposition.[4–6] We have been able to control the amount of bubble incorporation in the deposit through choice of a DC pulse of suitable size and duty cycle. In this paper we present the underlying mechanism involved for particle coagulation during pulse EPD.

Although EPD is used extensively for various applications over the years and several mechanisms have been proposed to explain experimental results of continuous DC EPD, a full understanding is still lacking. The main question that remains to be answered pertains to the particle coagulation mechanism during EPD. It is now recognized that EPD is a two step process: (i) first the particles in the suspension must migrate to the deposition electrode, and (ii) the particles must be destabilized to form the

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deposit on the electrode surface. The mechanism of particle stabilization and electrophoretic migration is now well established in the literature. However a general consensus pertaining to particle destabilization near the electrode has not yet been reached. According to Van Tassel and Randall,[7] there is no single mechanism of electrophoretic deposition (EPD). Just as there are several mechanisms for creating a stable colloidal suspension there are several mechanisms by which particles can be destabilized to form an adherent deposit at the electrode surface. Particles can be brought to an electrode by electrophoresis, but if there is no difference between the suspension in the bulk and the suspension at the electrode, particles that are stable in the bulk will remain stable at the electrode. As a result there will be no deposition. However, by recognizing the electrochemical changes that occur at the electrode, it is clear that there are many ways to change the nature of a suspension so that particles that repel in the bulk can be made to deposit at the electrode. Van Tassel and Randall[7] have given an overview of how particles come into contact with each other to form a rigid particulate structure. They summarized the mechanisms on the basis of densification, direct electrostatic force, electrosedimentary, ion depletion enhanced electrostatic, salting out, charge reduction/neutralization, squeezing out, bridging flocculation and desorption of neutral/charge polymer, polyelectrolyte neutralization. Several reviews on the mechanism and kinetics of EPD and the application thereof to ceramics have been published.[2,8,9] As per Zhitomirsky's analysis,[10] the EPD mechanisms can be divided into three categories: (i) charge neutralization or electrocoagulation, (ii) zeta-potential lowering, and (iii) particle accumulation. Hamaker and Verwey[11] pointed out that successful EPD need stable suspension and observed that when the suspension is allowed to stand undisturbed, it produced strongly adherent sediment. Therefore they suggested that the formation of deposit by electrophoretic deposition is similar to formation of sediment by gravitation and that the primary function of the applied electric field is to move the particles towards the electrode to accumulate. The pressures exerted by the incoming particles enable particles next to the deposit to overcome the interparticle repulsion. But this mechanism is feasible only for deposition on a dialysis membrane and not for deposition on an electrode. Grillon et al.[12] suggested that the particles would neutralize upon contact with the deposition electrode and then become static. But this mechanism explains only the initial stage deposition from dilute suspension and is invalid when (i) EPD is conducted for longer duration, (ii) particle–electrode processes are prevented, e.g. semi-permeable membrane induces deposition between the electrodes, and (iii) reactions occur at the electrode which alters the pH thereabout. Koelman[13] suggested electrochemical particle coagulation mechanism according to which the interparticle repulsion decreases near the electrode due to increase in electrolyte concentration near it leading to aggregation and consolidation of particles. This mechanism is applicable only when the electrode reaction generates $OH^-$ ions and is invalid when there is no increase of electrolyte concentration near the electrode. The most accepted mechanism of EPD until now is the one based on electrical double layer distortion and thinning proposed by Sarkar and Nicholson.[8] They suggested that during electrophoresis of particles, the shear force between the envelope of double-layer around the particle and the bulk fluid streamlines the double-layer, thinner ahead and wider behind, the particle. They speculated that the cations (co-ions) in the suspension which also move along with the positively charged particle towards the cathode, are in excess and react chemically with the counter-ions of the extended double layer tail, thus reducing its thickness and facilitating particle coagulation. But Sarkar and Nicholson[8] presented no experimental data to support their speculative mechanism of particle coagulation during EPD.

Following this, De and Nicholson[14] noted that as the cations carry the majority of current to the cathode, their concentration in the vicinity of the cathode must decrease because of discharge. This situation is counter to the Sarkar and Nicholson[8] mechanism and thus the real coagulation process must include a decrease of co-ion concentration as a function of position and time in the EPD cell. Koelman[13] calculated the expected increase in ionic strength next to an electrode and found that the ionic strength was of the same order as required to flocculate a suspension. De and Nicholson[14] developed a model and indeed showed through their calculation using the fundamental characteristic properties of powder, solvent, current densities etc that ions moving with the particles in suspension are depleted at the deposition electrode, locally changing the pH towards the isoelectric point ($pH_{iep}$) to facilitate coagulation. When a constant DC current is applied across an EPD cell, the free energy is no longer uniform or minimum everywhere. The resulting free-energy gradient sets up a drift (flux) of ions in a preferred direction (e.g. $H^+$ towards the cathode). This flux results in flow of charge in the electrolyte solution. In the absence of this drift, the electrode would soon run out of ions for necessary charge-transfer reactions. The $H^+$ must be supplied by the bulk solution ($x = \infty$) to the cathode interface ($x = 0$), so the charge transfer process involves two steps as shown below:

$$H^+_{x=\infty} \xrightarrow{\text{transport process}} H^+_{x=0} + e^- \xrightarrow{\text{charge transfer}} 1/2H_2 \qquad (1)$$

If the charge transfer process is at virtual equilibrium, the process will be controlled by the rate of diffusion of $H^+$ from the bulk to the interface. If the charge transfer process at the electrode consumes $H^+$, its concentration at the solution/electrode interface will drop below the bulk value. Their calculation also predicted the co-ion concentration gradient as a function of location within the suspension and the deposition time and its role in the coagulation process during EPD. But again, no experimental data were presented to support their calculation. A survey of literature also revealed no evidence of direct experimental verification of this mechanism. Therefore, we made an attempt to measure pH changes near the electrodes with a view to experimentally verify the pH localization mechanism of EPD.

## 2. Experimental

α-Alumina ($Al_2O_3$) powder (Sumitomo AKP-50) with average particle size of 0.20 μm and isoelectric point at pH 7.9, was used to first demonstrate the applicability of pulsed DC instead of continuous DC to obtain bubble free deposits during EPD

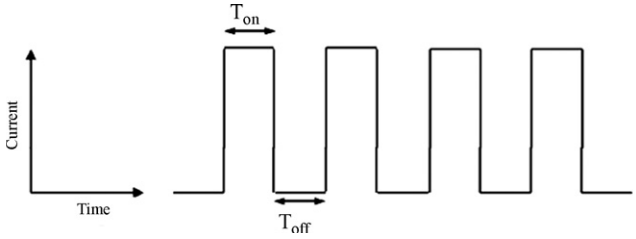

Fig. 1. A typical current pulse of 50% duty cycle.

from aqueous suspension. Well dispersed suspension of 5 vol% solids loading in distilled water was made by ultrasonication at 1200 W for 10 min to break up the agglomerates. The pH of the suspension was adjusted by nitric acid and sodium hydroxide. The details of pulsed DC EPD experimental methods have already been discussed in our earlier publications.[4,5] Stainless steel (316 L) plates of 2 cm × 5 cm × 0.4 mm dimension were used as deposition as well as counter-electrode.

Pulsed EPD was conducted at constant voltage and constant current mode by application of a series of direct current pulse of equal amplitude separated by periods of zero current, using a source meter (Model 2611, Keithley Instruments, Inc., USA). Simple square-wave pulses of desired duty cycles were used. The duty cycle (d.c.) of the pulse [i.e. $\text{d.c.} = T_{on}/(T_{on} + T_{off})$] was varied by keeping the pulse ON time ($T_{on}$) constant and varying the pulse OFF time ($T_{off}$). Fig. 1 shows a typical current pulse wave of 50% duty cycle. Unless and otherwise mentioned, deposition was carried out on a suspension at pH 4.5 for a total pulse ON time ($T_{on}$) of 3 min. It must be noted that the actual time of experiment was much more than 3 min and increased with decrease in pulse width. The influence of pulse width and duty cycle on deposit yield and quality was studied. The obtained deposits were dried overnight in air at room temperature and weighed together with the substrates to determine the deposit weight. The deposit quality was examined macroscopically by optical photographs recorded using a stereomicroscope.

To know the change in co-ion ($H^+$) and counter-ion ($OH^-$) concentration near the electrode, we first conducted a simple electrolysis experiment using distilled water in absence of any powder in it. The pH of the water was adjusted to 4.5 and ionic strength was kept constant by maintaining a conductivity of 110 μS/cm adjusted using 1.65 M NaCl solution to simulate the properties of a 5 vol% alumina suspension at pH 4.5. The electrode area was 4 $cm^2$ and the inter-electrode distance was 2 cm, and was same as that for the pulsed DC EPD. About 50 μl water sample was drawn carefully with a micro-pipette with sharp tip from near the wall of both cathode as well as the anode at different time interval ranging from 30 s to 10 min. It was carefully dropped onto an ion sensitive field effect transistor (IS-FET) pH meter (Model pH BOY® P2, Shendengen Electric Manufacturing Co., Ltd., Tokyo, Japan) as shown in Fig. 2. The electrodes are compactly housed at the tip of the pH meter. The 50 μl water sample was enough to reproducibly give a measure of pH which is displayed digitally. At least two measurements were made for each point.

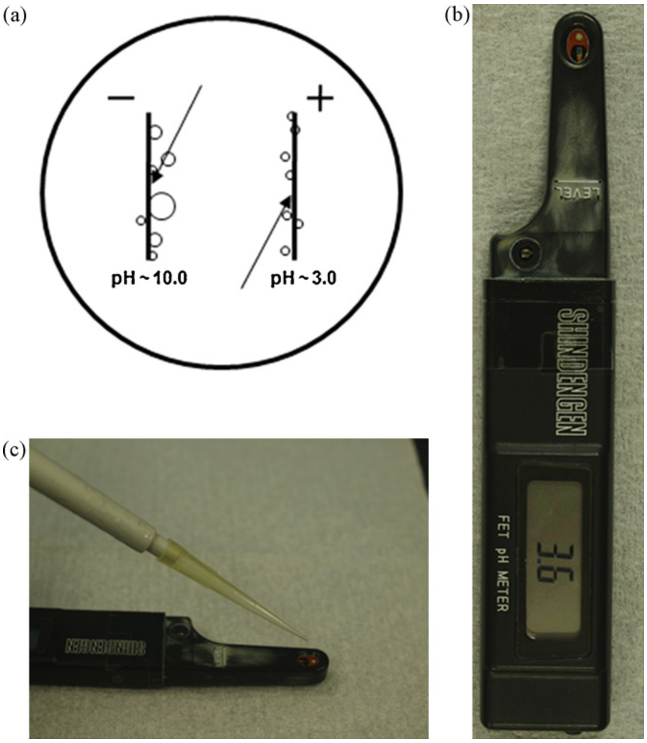

Fig. 2. Method of pH measurement near the electrodes during electrolysis. (a) Electrolysis bath showing bubble generation at the electrodes. Samples were drawn from the electrode surface from near the arrow head. (b) Special type of pH meter with micro-electrodes with which 50 μl sample is enough to give a reproducible measure of pH. (c) Electrolyzed water sample being dropped onto the microelectrode for pH measurement.

## 3. Results and discussion

### 3.1. Yield and deposit morphology

Pulse EPD experiments were conducted at both constant voltage as well as constant current mode. The deposit yield by constant voltage cathodic pulse EPD at 20 V applied potential for 3 min is shown in Fig. 3 and the corresponding surface morphology of the deposits is shown in Fig. 4. The pulse width of 180 s shown in Fig. 3 corresponds to continuous DC voltage applied for 3 min. It is evident that maximum deposition occurs on application of continuous DC. The yield decreases progressively with decrease in pulse size. The surface morphology of deposits obtained at continuous DC exhibit maximum incorporation of bubbles. The amount of bubble incorporation decreased on application of pulsed DC. In general, more bubbles were found on deposits formed with high pulse width than those formed at low pulse widths. There also exists a critical pulse size below which the deposit is free from any macro bubbles. But decreasing the pulse size to extremely low value leads to no deposition. There is a range of pulse width within which bubble-free deposits are obtained. At pulse width above this range, the deposit invariably contained incorporated bubbles whereas no deposition occurred below this range. Similar observations were made for pulsed EPD in constant current mode conducted at 0.004 A applied current (Fig. 4).

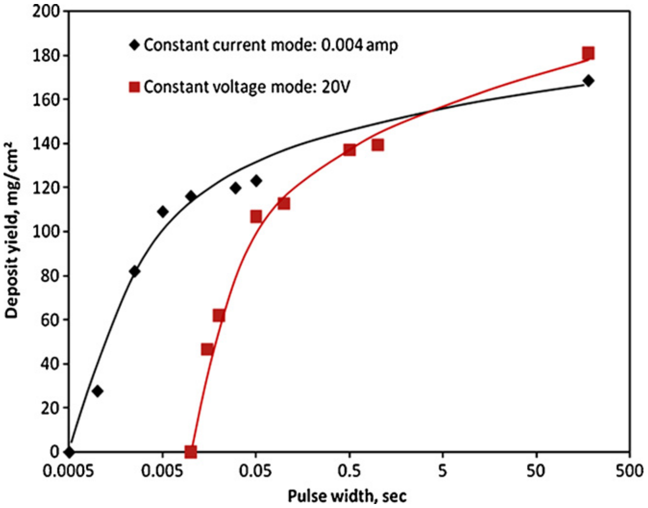

Fig. 3. Deposit yield as a function of pulse width [suspension: 5 vol%; pH. 4.5; pulse duty cycle: 50%].

### 3.2. Mechanism

We have successfully demonstrated that application of pulsed DC instead of continuous DC enables obtaining bubble-free deposits during electrophoretic deposition (EPD) from aqueous suspension. In addition the amount of bubble incorporation in the deposit could also be controlled through a judicious choice of pulse width and duty cycle. But the involved mechanism is not understood clearly. The primary questions that confronts us for pulsed EPD are: (i) what makes the particles migrate towards the deposition electrode during OFF time ($T_{\mathrm{off}}$) of the pulse when the applied current is zero, and (ii) why bubble incorporation decreases on application of pulse current, (iii) how do the particles coagulation happen at the deposition electrode, and (iv) why do the deposit yield decrease with decreasing pulse width. The answer to the first two questions were addressed in our previous publications.[4,5] It is perceived that when continuous DC is applied, the mass transport of particles due to the electrophoretic effect and their deposition at the electrode is a continuous process. During pulsed EPD, the mass transport of the particles from bulk suspension towards the electrode surface is likely to continue even during the current interruption due to their inertia of mobility caused by the effect of preceding current ON duration ($T_{\mathrm{on}}$). The continuity in mass transport during $T_{\mathrm{off}}$ was verified using Microelectrophoresis Apparatus Mark-II (M/s. Rankbrothers Ltd., UK) with provision for a video display. The particles continued to move across the grids in the video monitor towards the electrode of opposite polarity for a few more seconds after switching off the DC supply before it finally stopped moving.

To explain the decrease in bubble incorporation on application of pulsed DC, the following two possibilities were suggested

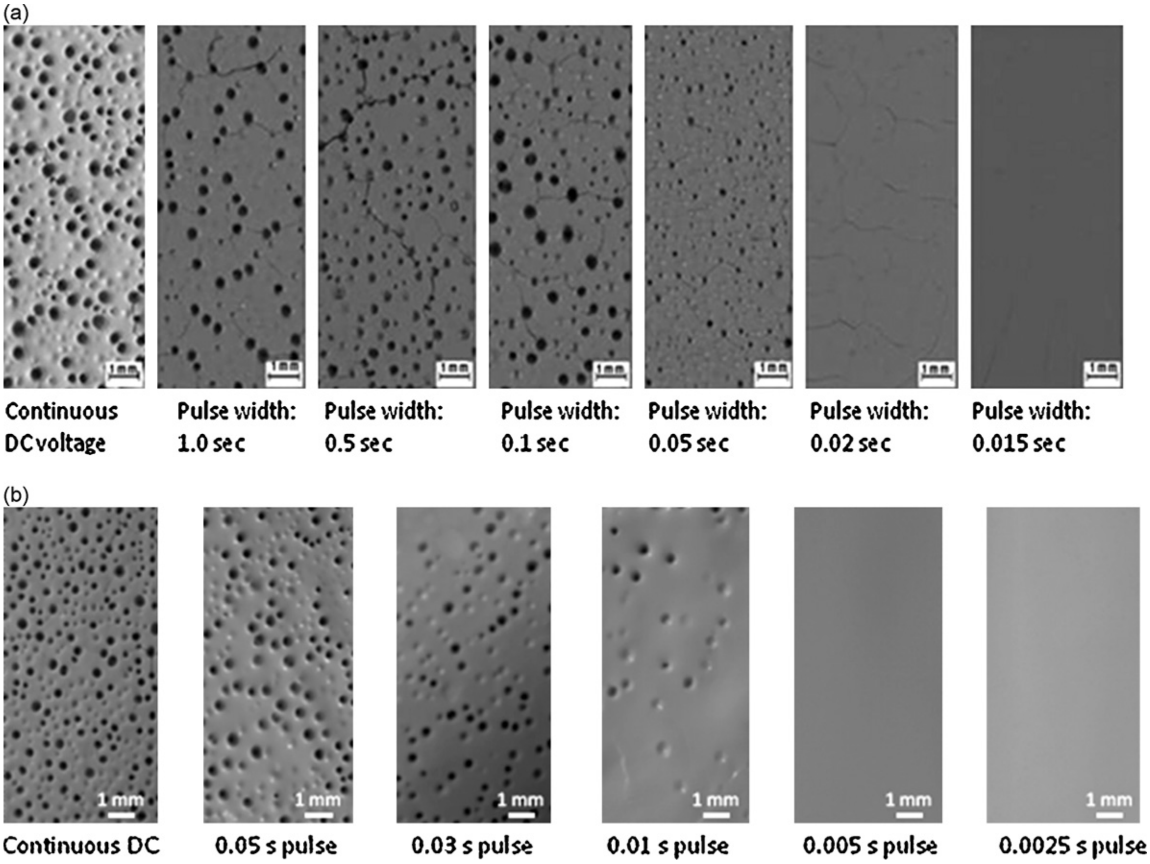

Fig. 4. Surface morphology of deposits obtained by pulsed DC EPD (a) in constant voltage mode at an applied voltage of 20 V, and (b) in a constant current mode at an applied current of 0.004 A [suspension: 5 vol%; pH 4.5; pulse duty cycle: 50%].

in our previous publications[4,5]: (i) the hydrogen or oxygen emitted at the electrode interface might be partly diffused away from the substrate during the duration of current interruption ($T_{off}$) and suppressed from being incorporated in the deposit during pulse EPD,[15,16] (ii) the discrete amount of gas generated by electrolysis of water during each ON time ($T_{on}$) of a pulse is expected to be significantly less compared to a single continuous DC. Theoretically, a summation of the gas generated by all the pulse for a total ON time may be same as the total gas evolved by electrolysis of water on application of continuous current. However, since the pulsed DC consists of an OFF time in each cycle, the actual time elapsed is much more than the time required to apply continuous DC depending on the pulse size and duty cycle. Under this circumstance, a large fraction of the generated gas would have dissolved and dissipated in water on completion of the pulse ON time. Therefore it will be more practical to measure the amount of gas present at any given time rather than measuring the amount of gas evolved under continuous and pulsed current. Concurrently, while a continuous DC application is completed in 3 min, the ON time of pulse DC applied for the same duration is infact much less than 3 min. Therefore the amount of gas evolved at a given time for pulsed DC is expected to be much less compared to continuous DC. We believe that the gas evolution and dissipation in the case of pulse current electrolysis is a dynamic process in which the gas nucleation sites on the electrode surface for a pulse keep changing and may be different from the preceding and succeeding ones. Such a scenario will lead to formation of many micro and nanosized bubbles uniformly distributed throughout. Incorporation of such small bubbles will not produce any macro-bubbles in the deposit. Kikuchi et al.[17] observed that in electrolyzed water, the hydrogen nanobubble concentration started to decrease immediately after electrolysis and disappeared within 3 h. The rate of decrease in concentration of hydrogen nanobubble below 600 nm and dissolved hydrogen with elapsed time after electrolysis was independent of ionic strength, ion type and storage temperature. Therefore, Kikuchi et al.[17] concluded that the reason for the decay was not coalescence but, rather, the dissolution of hydrogen molecules from the bubbles into solution. It was found that nanobubbles do not grow into larger bubbles that leave the solution, but dissolve into the bulk solution. Tanaka et al.[18] observed that smaller the size of the bubbles, faster is the dissolution and transfer of hydrogen from the bubbles into the bulk. Since it is known from electrochemistry that Ampere × time = Coulombs; 96,485 Coulombs = 1 Faraday; and 1 Faraday = 1 mole of electron, we made an estimate of the theoretically possible amount of hydrogen generation during each pulse ON time ($T_{on}$) for all the pulse widths from the decomposition reaction of water in which 2 moles of electrons produced 1 mole of $H_2$ gas. It was shown in our previous work[5] through such theoretical estimation that the discrete amount of $H_2$ generated at an applied voltage is maximum for continuous DC compared to a single ON time of a pulse because of the smaller size of each ON time. The summation of all the pulse should produce the same amount of $H_2$ gas as a single continuous DC. But as already mentioned earlier, a large fraction of $H_2$ evolved by pulse current would have dissolved away. The amount of $H_2$ evolution decreases on application of pulse voltage. Larger the pulse size higher is the evolved $H_2$ per single ON time and slower is its dissolution and transfer into bulk compared to smaller pulse. So the incorporation of bubbles for larger pulse is likely to be higher compared to smaller pulse. In our previous publication[5] we have made a direct experimental verification of $H_2$ evolution and its presence during electrolysis of distilled water by continuous and pulsed current by monitoring the gain in weight of a palladium (Pd) cathode suspended into the electrolysis bath from an electronic analytical balance. Since palladium (Pd) is known to absorb hydrogen, the gain in weight of the Pd electrode can be directly attributed to the amount of hydrogen absorbed on it. A linear increase in weight of the electrode was noticed with increasing time. As expected, maximum weight gain was noticed in the case of continuous current and it decreases progressively with decrease in pulse size. It was also noticed that the weight gain at the end of the total pulse ON time of 3 min for different pulses are not equal to that due to continuous current. It decreases with decrease in pulse size. Therefore, it is possible that not all the hydrogen evolved is absorbed by the palladium electrode. A fraction of the evolved hydrogen may have been dissolved and dissipated away.

We found that the coagulation of particles at the electrode and decrease in deposit yield with decreasing pulse width can be explained easily with the aid of De and Nicholson's[14] charge transfer process given by Eq. (1). Since the charge transfer process at the electrode consumes $H^+$, its concentration at the solution/electrode interface will drop below the bulk value. Also evolution of hydrogen as gas bubble at the cathode will decrease the total concentration of hydrogen at the solution/cathode interface. So the local pH near the cathode is expected to increase. Similarly, the evolution of $O_2$ at the anode/solution interface will decrease the concentration of $OH^-$ there. So a decrease in pH is expected at the anode/solution interface. The measured value of local pH at cathode/solution and anode/solution interface during constant voltage electrolysis of water with bulk pH 4.5 at an applied voltage of 20 V is shown in Fig. 5. The experimental data clearly show a substantial increase in local pH at the cathode/solution interface (Fig. 5a) and a marked decrease in the local pH at the anode/solution interface (Fig. 5b). The rise in pH was maximum and reached as high as 10.7 on application of 20 V continuous DC. The rise in pH was very rapid and reached the plateau value of pH 10.7 in 30 s. Further increase in electrolysis time did not increase the pH any further. The rise in pH was gradual on application of pulse voltage. The plateau value of pH decreased with decreasing pulse size. Also longer electrolysis time was needed to attain the plateau pH with decreasing pulse size. The rise in pH for a pulse size of 0.001 s for 20 V applied potential was negligible. The local pH at the anode/electrolyte interface dropped from bulk pH to as low as pH 2.9 within 30 s of electrolysis on application of continuous voltage of 20 V. Further increase in electrolysis time did not decrease the pH any more. The decrease in pH was less on application of pulse voltage. Lower the pulse size less was the decrease in anode/solution interface. Similar trend of increase in pH at the cathode/solution interface and decrease in pH at the anode/interface was observed for constant cur-

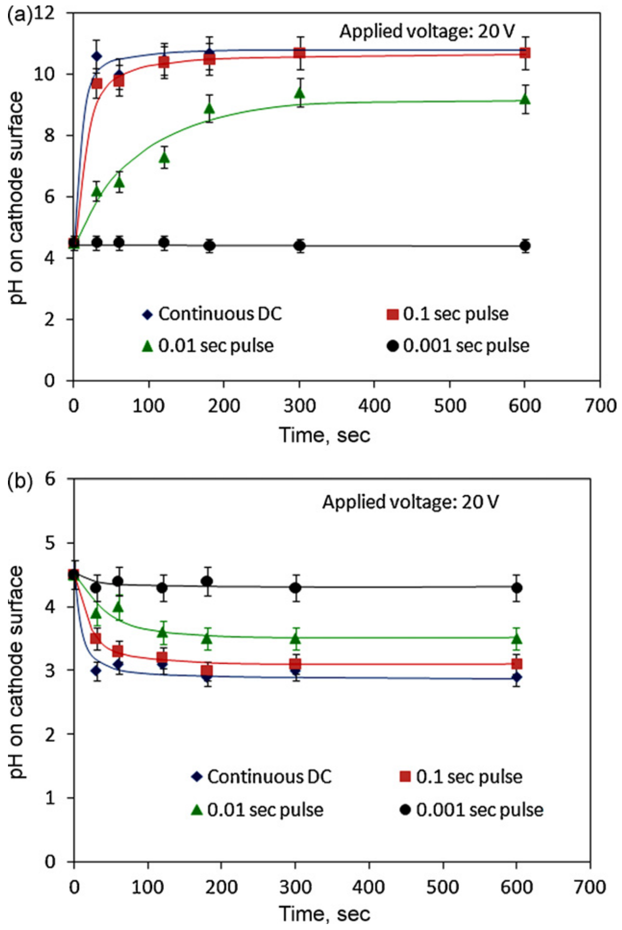

Fig. 5. pH localization during constant voltage electrolysis of water at (a) cathode/solution interface, and (b) anode/solution interface [initial bulk pH 4.5, conductivity = 110 $\mu$S/cm; applied voltage = 20 V].

rent electrolysis conducted at an applied current of 0.004 A (Fig. 6).

The change in local pH near the electrode/solution interface has a significant influence on coagulation of particles during electrophoretic deposition (EPD). For alumina suspension, if the pH shifts from its bulk value of 4.5 to alkaline side on application of electric field, it will tend to reach the isoelectric point ($\mathrm{pH_{iep}}$). The moment the local pH near cathode/solution interface reaches $\mathrm{pH_{iep}}$, the suspension will spontaneously coagulate because of strong van der Waals attraction forming the deposit on the cathode. Since the attainment of plateau pH at the cathode/solution interface is fastest for continuous DC, one can expect to reach the $\mathrm{pH_{iep}}$ earlier and closer for continuous DC than pulsed DC. Similarly, application of larger pulse will tend to reach the $\mathrm{pH_{iep}}$ earlier and more closer than smaller pulse. Therefore, maximum deposition is expected for continuous DC and will decrease progressively with decrease in pulse size. This is in agreement with the experimental results shown in Fig. 3.

To verify if the pH localization at the electrode/solution interface is the valid underlying mechanism for coagulation of particles during an actual electrophoretic deposition (EPD) process, we conducted EPD experiments on 5 vol% alumina suspension maintained at pH 4.5. But unlike in a water electrolysis experiment, it was difficult to draw sample for pH measurement during EPD experiment because of formation of an adherent deposit on the cathode. In this case, after completion of the deposition time, the deposited mass was immediately taken out from the EPD bath and scrapped off quickly before it start to dry. The scrapped off lump was then smeared on the micro-electrode of the pH meter. Measurement of pH in this manner was very reproducible. The results reported in this paper are an average of 2 measurements. Table 1 gives the result of pH of deposited mass obtained at applied oltage of 20 V and

Table 1
pH of alumina deposited at cathode on application of 20 V for 3 min [suspension: 5 vol%, bulk pH 4.5].

| Sl No | Pulse size | pH of deposited mass at cathode | Deposit yield, mg/cm$^2$ | pH at anode |
|---|---|---|---|---|
| 1 | Continuous DC | 8.4 | 180.77 | 4.5 |
| 2 | 0.1 s pulse | 6.9 | 112.55 | 4.5 |
| 3 | 0.01 s pulse | 5.4 | 46.50 | 4.6 |
| 4 | 0.001 s pulse | – | 0.00 | 4.6 |

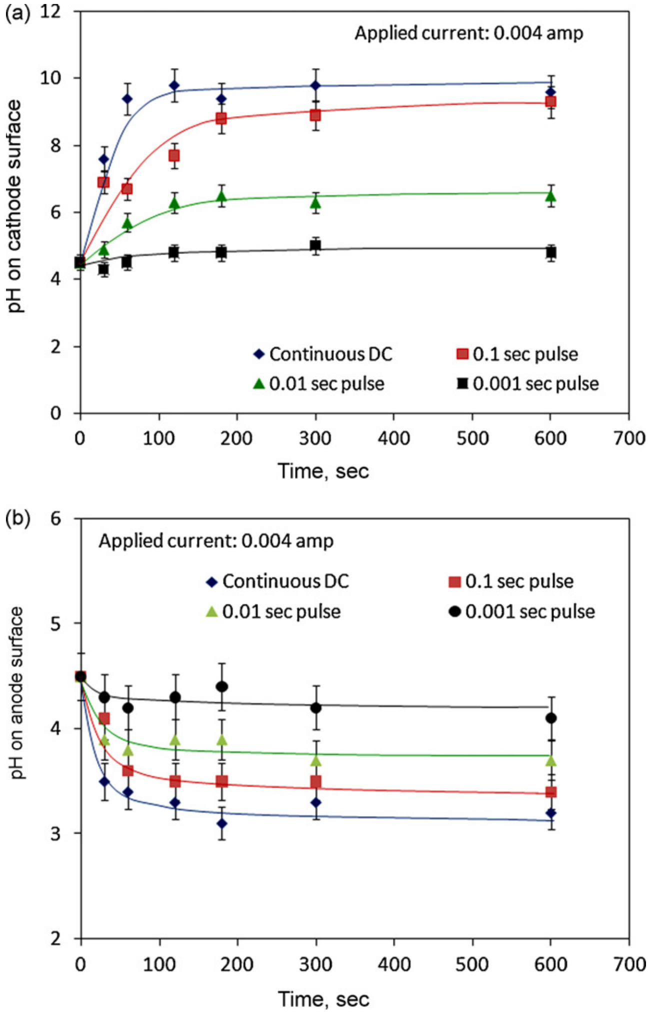

Fig. 6. pH localization during constant current electrolysis of water at (a) cathode/solution interface, and (b) anode/solution interface [initial bulk pH 4.5, conductivity = 110 $\mu$S/cm; applied current = 0.004 A].

depositin time of 3 min. It shows that the pH of the deposited mass on application of continuous DC was closest to the $pH_{iep}$ of 7.9 and corresponds to maximum deposition yield. The pH decreased progressively with decreasing pulse size resulting in concurrent decrease in the deposit yield because the attainment of local pH became farther away from $pH_{iep}$. The results are in agreement with the conclusions drawn from electrolysis experiments. However, it must be noted that unlike in the electrolysis experiment where the pH of cathode increased to as high as 10.7 for continuous DC, the increase in cathode pH in a real EPD experiment in presence of alumina powder was upto 8.4 only. The change in pH of anode was very negligible for continuous as well as pulsed DC and it remained more or less at the same pH value of 4.5. It appears that the presence of powder limits the change in anode as well as cathode pH (Fig. 6)

## 4. Conclusions

The pH localization mechanism of particle consolidation during electrophoretic deposition (EPD) proposed by De and Nicholson[14] have been experimentally verified for aqueous suspension. The electrolysis experiments in absence of any powder showed a substantial increase in pH at cathode/solution interface on application of electric field because of depletion of hydrogen concentration there. The increase in pH was maximum on application of continuous DC and it decreased progressively with decreasing pulse size. Simultaneously, a decrease in pH was noticed at the anode/solution interface during electrolysis. The concept was verified in a real EPD experiment using 5 vol% alumina suspension with bulk pH maintained at 4.5. On application of a constant voltage of 20 V, the pH near the cathode/solution interface was shifted towards isoelectric point (pH 7.9). The kinetics and closeness of attainment towards i.e.p. was maximum for continuous DC and it decreased progressively with decreasing pulse size. There was a concurrent decrease in deposit yield with decreasing pulse size.

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