Effect of cationic charging agent on the bonding strength of coarse Titanium particles deposited by electrophoretic deposition

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ABSTRACT

Electrophoretic deposition (EPD) is a potential coating technique for surface hardening of steel when combined with a subsequent rapid sintering process. This process requires synergy between suspension particles and charging agent, particularly when the particles involved are noncolloidal in nature. The present work will investigate the effect of three commercially-available cationic charging agents; aluminium (III) chloride ($AlCl_3$), polyethyleneimine (PEI) and poly (diallyldi-methylammonium chloride) (PDADMAC) on the EPD of coarse Ti particles onto steel. Surface microstructure, deposit yield, electrophoretic mobility and electrical conductivity were used to characterize Ti particles and obtained Ti deposit. The key finding of the present study is the bonding strength of charging agent-adsorbed coarse Ti particles deposits predominantly controlled their deposit yield. Electrophoretic

mobility of the Ti particles only played a lesser role in the deposit yield because of strong hindrance of gravity on the moving coarse particles. Charging agent, which gave the strongest to the weakest bonding strength is as follow: $AlCl_3$, PDADMAC (M_w = 100,000 -200,000 amu), PDADMAC (M_w = 400,000 -500,000 amu), PEI.

Keywords: Titanium Particles, Electrophoretic Deposition, Bonding Strength, Coating, Polyelectrolyte

1.0   INTRODUCTION

Electrophoretic deposition (EPD) has a potential to become an alternative coating technique for various applications, mainly because of its feasible equipment set-up and good control in the coating process and thickness of simple or complex shapes [1-4]. EPD technique has been rarely considered as an alternative to the commercially available coating techniques for surface hardening because of the deposited coating is weak in terms of mechanical strength and bonding to the supporting substrate, [1, 4]. Nevertheless, combinations of this method with a subsequent heat treatment method were able to increase density and strengthen the EPD coating for the corrosion protection application [4, 5].

Titanium (Ti) metallic particles are normally used in the powder metallurgy of Ti-based alloys, and also in many other applications owing to its low true density, high strength, ductility, and high corrosion resistance [6, 7]. However, Ti particulate coating (e.g., coating of deposited particles) applied on steel by the EPD could serve as a controllable layer of Ti reservoir for the formation of abrasive Ti-based (such as TiN, TiC) coating on the steel surface if the Ti-coated steel undergoes further heat treatment in reactive gas environment (e.g., NH_3, CH_4).

EPD of Ti particles requires the usage of charging agent to provide additional surface charge for the stabilization and electrophoretic mobility of suspension particles and also for their deposition process [1, 4, 8]. Most importantly, these charging agents also act as binders to increase bonding between the deposited particles and bonding with the substrate [1, 4, 8]. The commonly used charging agents for the EPD of metallic particles were aluminium chloride ($AlCl_3$) [5, 9], poly (diallyldimethylammonium chloride) (PDADMAC) [10, 11] and polyethyleneimine (PEI) [12, 13]. Although the effect of these charging agents had been extensively conducted by these studies, a direct comparison of the effect of these charging agents on the EPD of Ti particles has never been reported. Furthermore, there is a lack of discussion on the role of these charging agents on the mechanism of electrophoretic deposition, particularly on the noncolloidal coarse particles.

The objective of the present work was to compare and investigate the effect of aluminium (III) chloride ($AlCl_3$), polyethyleneimine (PEI), poly (diallyldimethylammonium chloride) (PDADMAC)] on the EPD of coarse Ti particles in absolute ethanol medium. The effect of the charging agent on the bonding strength EPD will be deduced based on the following criteria: (i) planar surface microstructure of the Ti deposit, (ii) deposit yield, and (iii) electrophoretic mobility of the Ti particles.

2.0   EXPERIMENTAL PROCEDURE

2.1   Preparation of Suspension

The as-received Ti particles (99.7 wt%, SE-Jong Materials Co. Ltd., South Korea) used for the current study was platy, subangular, and of medium sphericity. Their particle size range was ~1-50 μm, with a median size (d_{50}) of ~17 μm. Suspension was prepared by adding 0.1 g of Ti powder to 20 mL of absolute ethanol

(99.7 wt%, CSR Ltd., Australia) to give a solids loading of 5 mg.mL^{-1}. After magnetically stirred gently for 1 min, small amount of a selected charging agent (0.1-0.7 wt% from Ti particles weight basis) was added and followed by magnetic stirring for 30 min at the same stirring speed. The temperature of the suspension was maintained at ~25°C throughout the preparation process.

Table 1: Details of charging agents used for EPD of Ti particles (all the chemicals are reagent grade and were supplied by Sigma-Aldrich Co., Australia)

Charging Agent	Average Molecular Weight (amu)	True Density (g.cm^{-3})	Concentration prior to Addition into Suspension Medium	Symbol
Aluminium (III) Chloride	N/A	2.44	0.375 M in water	AlCl$_3$
Polyethyleneimine	10,000-25,000	1.03	10^{-2} M in absolute ethanol	PEI-10K
Polyethyleneimine solution	60,000-750,000	1.04	50 w/v% in water	PEI-60K
Polyethyleneimine solution	600,000-1,000,000	1.04	50 w/v% in water	PEI-600K
Poly(diallyldimethyl ammonium chloride) solution	100,000-200,000	1.04	20 wt% in water	PDADMAC-100K
Poly(diallyldimethyl ammonium chloride) solution	400,000-500,000	1.04	20 wt% in water	PDADMAC-400K

N/A: Not applicable

For the suspension using PEIs as the charging agents, small amount of acid was added as the protonating agent of the amine functional groups in the PEI polymers [16]. List of Ti particles suspensions prepared using different cationic charging agents are shown in Table 1. Further description of the Ti particles and ethanol used in the current work had been stated in the previous work [15].

2.2   EPD Process

The circuit in the EPD set-up consisted of mutually parallel electrodes at a fixed separation, connected by alligator clips to a d.c. programmable power supply (EC2000P, E-C Apparatus Corp., USA). The cathode (working electrode) or substrate consisted of SAE 1006-grade low-carbon steel, the anode (counter-electrode) consisted of 304 grade stainless steel. Both the electrodes have submerged dimensions of 10 mm H × 10 mm W × 1.5 mm T and were supplied by BlueScope Steel Ltd., Australia. The low-carbon steel substrates were hand-polished to P320-grit (46.2 μm particle size) SiC paper, ultrasonically cleaned in absolute ethanol, and air-dried for 30 minutes before deposition. Each suspension was magnetically stirred for ~1 min following lowering of the electrodes into the suspension. After this, the voltage was applied. Each sample was removed from the suspension slowly at constant pulling rate of 0.2 mm.s^{-1} immediately after EPD ended.

2.3   Characterizations

Measurements were undertaken in terms of determination of the EPD yield (weight gain/total submerged surface area) as a function of addition level of charging agent. The weight gain was determined after EPD for each cathode by air drying for ~30 min and weighing (0.00001 g precision, BT25S, Sartorius AG, Germany). All of these deposit yield data are the averages of five individual measurements with standard error of approximately ±0.0001 g/cm^2. The particle and deposit morphologies as well as the general appearance of the deposits were assessed by scanning electron microscopy (SEM, 15 kV accelerating voltage, secondary electron emission mode, S3400N, Hitachi High-Technologies Corporation, Japan). The electrophoretic mobility

and electrical conductivity were determined using a phase-analysis light-scattering zeta potential analyser (ZetaPALS; sole setting of ~10 V.cm^{-1} electric field bias change with 2 Hz frequency sinusoidal wave, 0.005-30 μm size range, scattering light source [678 nm wavelength], Brookhaven Instruments Co., USA). All of these electrophoretic mobility data are the averages of ten individual measurements with standard error of approximately ±0.1 μm.cm/V.s.

3.0   RESULTS AND DISCUSSION

3.1   EPD's Deposit Yield and Bonding Strength

Previous studies shown that EPD deposit yield is governed by the deposition efficiency of the particles (e.g., mass ratio of total particles deposited over the total particles reaching electrode during EPD) [1, 4, 8]. It is interpreted that the amount of accumulation of deposition of particles (e.g., deposit yield or thickness of coating) on the substrate is controlled by the van der Waals bonding strength of the deposited particles. Disparity in bonding strength of Ti deposits prepared by different charging agents are exhibited by their respective areal deposit microstructure (refer Figure 1). Because of Ti deposit was oriented vertically during deposition and lifting after post-EPD, the Ti deposit was subject to detrimental gravity and suspension's adhesive pulling effect. Particle dislodgement will occur when there was a dominancy of gravity and adhesive force of suspension over the weaker inter-particles bonding (e.g., van der Waals). Therefore, the degree of particles dislodgement directly correlates with the bonding strength of the related deposit.
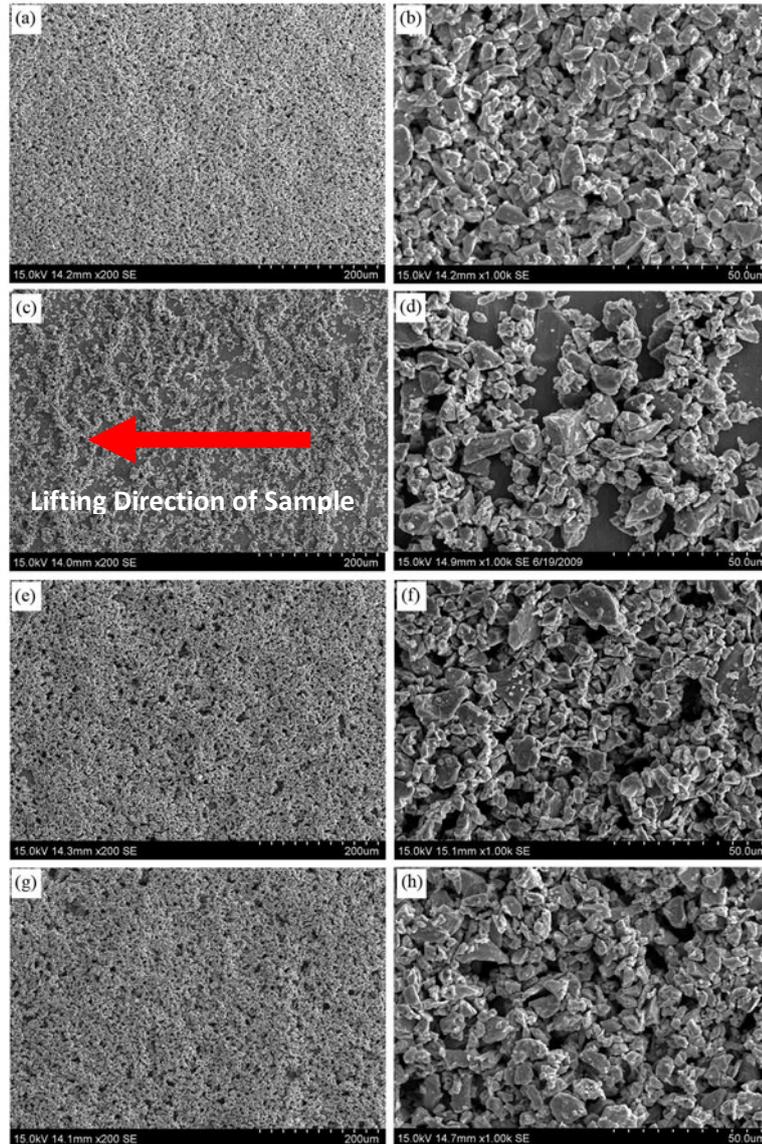
Figure 1: SEM micrographs of Ti deposits prepared using different charging agents. (a), (b): 0.3 mM AlCl$_3$; (c), (d): 0.3 wt% PEI with average molecular weight =10,000-25,000 amu mixed with 0.013 mM acetic acid protonating agent; (e), (f): 0.3 wt% PDADMAC with average molecular weight = 100,000-200,000 amu; (g), (h): 0.3 wt% PDADMAC with average molecular weight = 400,000-500,000 amu. (a), (c), (e), (g): ×200 magnification; (b), (d), (f), (h): ×1000 magnification. Lifting direction of the deposited steel substrate after EPD is shown in arrow in Figure 1(c)

Smooth deposit surface and negligible particle dislodgement were observed on AlCl$_3$-related deposit, thus implying a strong bonding strength deposit. However, particles dislodgement of large particles had occurred in PDADMAC deposits as

illustrated by the randomly distributed and micro-sized (= 10-20 μm) cavities on the deposit surface. This implies particle bonding strength in PDADMAC-derived deposit is weaker than in AlCl$_3$-derived deposit. However, there is less significant difference in the surface microstructure of deposit produced using PDADMAC with different molecular weights.

A much weaker bonding strength deposit was acquired when PEI was used as charging agent. This was illustrated by the low and wavy deposit coverage, thus suggests severe particles dislodgement irrespective of the deposited particle size. Moreover, the usage of PEIs with larger average molecular weights (PEI-60K or PEI-600K) was unable to prevent occurrence of the particle lodgement. It is believed that the current PEI-adsorbed Ti particles had a low surface charge, likely due to the weak ionic amine functional groups of the PEI and low ion dissociation of the protonation agent (e.g., acetic acid) in the absolute ethanol suspension medium. It is known that the dielectric constant of water is larger than the ethanol (dielectric constant of water is 80.4 and ethanol is 24.64 [17]), and has capabilities to promote ion dissociation of acids [18].

Lastly, EPD of suspension comprised of Ti particles and ethanol medium did not give any deposit on the substrate. A further addition of acid and water into the reference suspension sample also did not generate Ti particles deposition. The observation implies that the adsorption of charging agent on Ti particles enabled electrophoresis of Ti particles and also strengthened the bonding strength between deposited particles and with the substrate, thus generated Ti deposit yield.

Based on the qualitative comparison of the particle dislodgement from the deposits produced using different charging agents, it is suggested that the sequential arrangement of charging agent in terms of their corresponding bonding strength from

the strongest to the weakest are as follow: $AlCl_3$, PDADMAC-100K, PDADMAC-400K, PEI (e.g., PEI-10K, PEI-60K, PEI-600K).
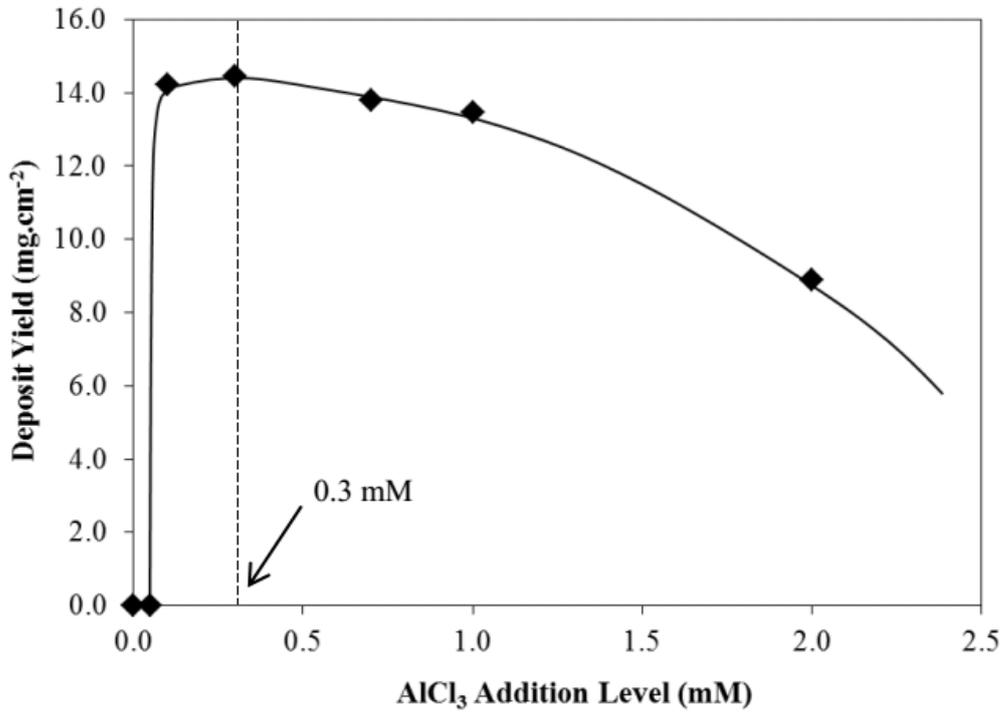

Figure 2: Dependence of the deposit yield on the $AlCl_3$ addition level [solids loading = 5 mg.mL^{-1}, deposition time = 5 min, applied voltage = 200 V, electrode separation = 1 cm]
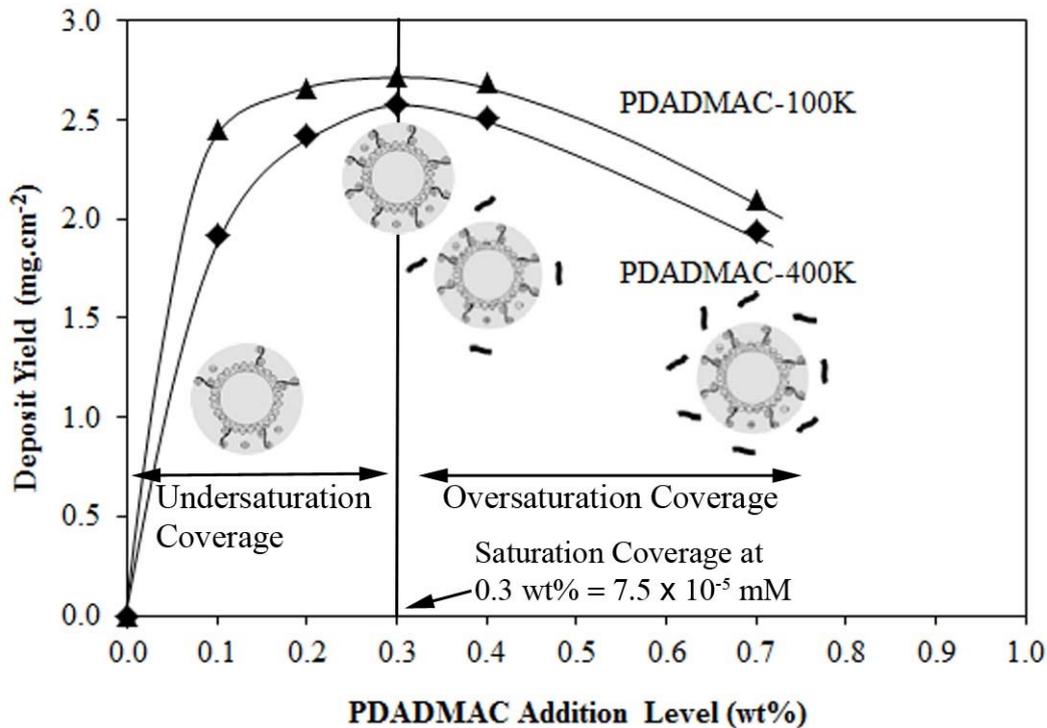
Figure 3: Dependence of the deposit yields on the addition levels of PDADMAC with average molecular weight of 100,000–200,000 amu and 400,000–500,000 amu. Schematic diagram of charging agent-adsorbed particles at different addition levels are also shown

3.2 EPD Deposit Yield and Electrophoretic Mobility

Graphs of deposit yield as a function of the addition levels (from 0 to 0.07 wt%) of $AlCl_3$, PDADMAC-100K and PDADMAC-400K were shown in Figure 2 and Figure 3. Deposit yield measurement was not conducted for PEI-added EPD because of large particles dislodgement during EPD. Thus, it is impossible to make a reliable comparison of deposit yield of PEI with the other charging agents. The Figure 2 and Figure 3 generally show the following similar profile: (i) At lower addition levels, deposit yields show a rapid logarithmic increase until the yield reaching its maximums at optimum addition level, and then (ii) followed by a slower logarithmic decline of yield at higher addition levels. A more detailed assessment of the deposit yield,

electrophoretic mobility and electrical conductivity of charging agent-adsorbed Ti

particles deposited by EPD had been discussed in detail in other paper [15, 19].

Previous studies had suggested that EPD deposit yield is also governed by the

electrophoretic mobility of suspension particles [1, 4]. Figure 4 and Figure 5 shows the

profile of electrophoretic mobilities of Ti versus the addition level of $AlCl_3$ and

PDADMACs, which are similar to the deposit yield profile. This suggests there is a

dependency of deposit yield on the electrophoretic mobility of Ti particles. However,

deposit yield measurement of $AlCl_3$ was comparatively higher than the PDADMAC-

100K and -400K (see Figure 2 and Figure 3), but their electrophoretic mobilities

measurements are comparable at below-optimum saturation addition level. These

results imply the electrophoretic mobilities of Ti particles did not have a significant

effect on the deposit yield. Electrophoretic mobility of the Ti particles only played a

lesser role in the deposit yield because of strong hindrance of gravity on the moving
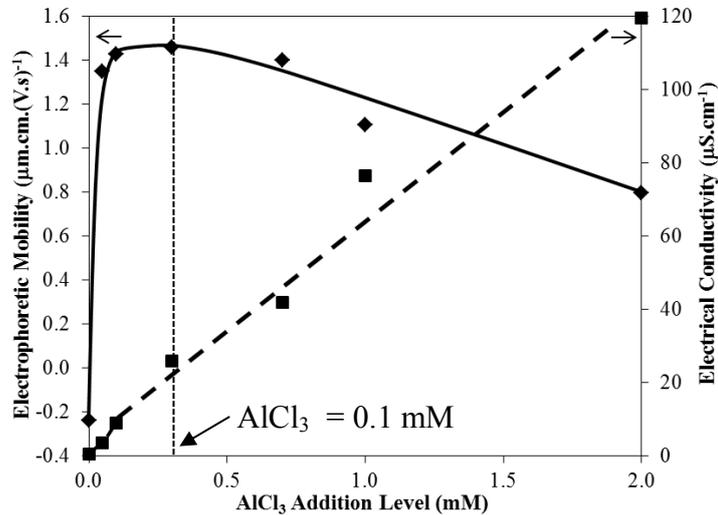
coarse particles.

Figure 4:   Electrophoretic mobilities of Ti particles and electrical conductivities of
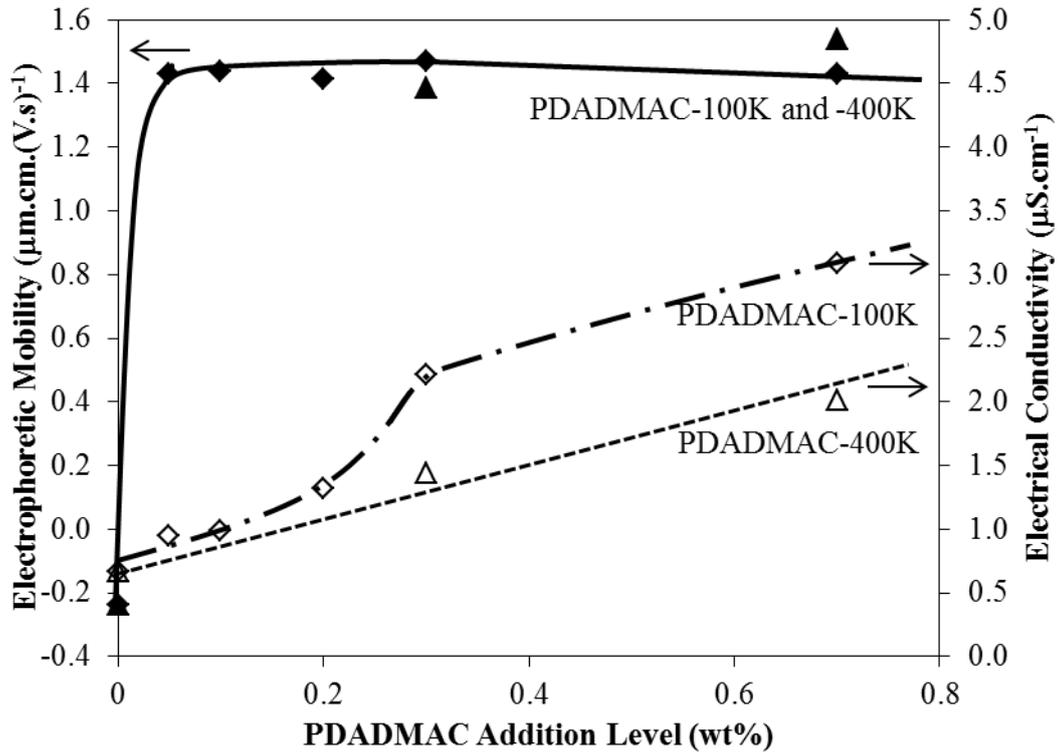   suspension as a function of $AlCl_3$ addition level

Figure 5: Electrophoretic mobilities (EM) of Ti particles (Symbol: ▲ and ◆) and electrical conductivities of suspension (Symbol: ◊ and Δ) as a function of addition levels of PDADMAC-100K (average molecular weight = 100,000–200,000 amu) and PDADMAC-400K (average molecular weight = 400,000–500,000 amu). Note: Curve fitting on the EM data of PDADMAC-400K was not conducted because of limited data points

It is proposed that the deposit yield varied because of different bonding strength of Ti particles attributed to the adsorbed charging agent. A higher surface charge density Al^{3+}-adsorbed Ti particles created a stronger interaction with the electric field and resulted in a denser packing density. A closer particles arrangement of the Al^{3+}-adsorbed Ti particles enhanced the van der Waal bonding, thus increased the deposition deficiency of the Ti particles. Whereas, lower packing density was expected for the high polymeric chain and relatively lower surface charge density PDADMAC-adsorbed Ti particles. Therefore, lower van der Waals bonding between the deposited particles and lower deposit yield were observed in the PDADMAC-adsorbed Ti particles.

Furthermore, excess (free) charging agent will be deposited in between the Ti particles as the addition level of charging agent increase more than the optimal addition level. The large polymeric size of interpose PDADMAC as compared to the small interpose Al^{3+} ion may cause larger particle dislodgement and/or higher electric field shielding effect, further decrease the bonding strength of deposit prepared by the former. Effect of charging agent's size and surface charge density on the deposit yields was also been exhibited where deposit yield corresponded to PDADMAC-100K (a smaller molecular size) was higher than the PDADMAC-400K (larger molecular weight).

4.0   CONCLUSIONS

Charging agent which gave the strongest to the weakest bonding strength of Ti particles deposit is as follow: $AlCl_3$, PDADMAC (M_w = 100,000 -200,000 amu), PDADMAC (M_w = 400,000 -500,000 amu), PEI (M_w = 10,000-25,000 amu; 60,000-750,000 amu, 600,000-1,000,000 amu). When a stronger charging agent was used, packing density of the deposited particles increased. The reduced separation of deposited particles increased the van der Waals bonding strength between the particles, thus improved bonding strength (e.g., represented by deposit yield) of the Ti particles on the depositing electrode. Meanwhile, the obtained deposit yield profiles (corresponding to $AlCl_3$ and PDADMAC) correlated well with their respective electrophoretic mobilities profiles. However, their deposit yield measurements varied although their respective electrophoretic mobilities measurements were almost equal. The lack of correlation between the maximum deposit yields and maximum electrophoretic mobilities indicates the dominancy of bonding strength factor over the electrophorectic mobility factor during the EPD of the charging agent-adsorbed coarse Ti particles.

ACKNOWLEDGEMENTS

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