

# Effect of Nano-Ceria on Physiognomies of Aluminum-5% Zinc Sacrificial Anode

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## ABSTRACT

Sacrificial anodes possessing higher electrochemical efficiency is the demand of marine, oil and gas industries. Due to high energy capability and long life light weight aluminum based anodes are more favorable as compare to magnesium and zinc based anodes to protect the engineering structures from corrosion. In present study an attempt was made to develop Al-5% Zn based composite with nano-ceria. The effect of nano-ceria on physiognomies of Al-5% Zn anode was determined through weight loss, CPR (Corrosion Penetration Rate) and emf study in CCP (Close Circuit Potential) conditions. The results indicated that by incorporating the ceria in the matrix of Al-5% Zn anode the corrosion inhibition efficiency and hardness were increased significantly.

**Key Words:** Nano Ceria, Aluminum-5% Zinc Alloy, Sacrificial Anode.

## 1. INTRODUCTION

Very often, the corrosion to be a major cause of deterioration of physico-mechanical properties of complex engineering structures is reported in the literature. To prevent structures from corrosion attack variety of techniques comprising electroplating, coating and painting, use of inhibitors, cathodic protection and anodic protection have been developed [1-3]. Among the list of the criterions used for the selection of the appropriate technique the location of the engineering structure and environment are the most critical parameters. Based on these criterions the cathodic protection technique is often selected for submerged

structures. Cathodic protection simply involves the supply of electrons from an external source to the structure to be protected. ICCP (Impressed Current Cathodic Protection) and SACP (Sacrificial Anode Cathodic Protection) are the sub types of cathodic protection [4-6].

Literature pertaining to SACP indicates that scarifying tendency of Al anode fails within short time due to its higher passivity character. To overcome the passivation problem and enhance the anodic efficiency Al anodes were alloyed with Zn, Mg, Cd, Ga, In, Hg and Tl metals. Efforts made so far revealed that addition of 5% Zn has

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improved the anodic efficiency of Al significantly as compared to other alloying elements. Study of various researchers indicates that appreciable improvement in the Al-5% Zn anode is caused by the formation of  $\beta$ -phase [7-10].

Although, by addition of 5% Zn the sacrificial tendency of Al was improved sufficiently, even though Al-5% Zn anodes have not gain much industrial attraction because of its non-columbic loss and microbiologically induced corrosion attack in aqueous environments. Shibli et. al. [9-11] observed that addition of various metal oxides (such as  $\text{IrO}_2$ ,  $\text{RuO}_2$ ,  $\text{CeO}_2$  and  $\text{ZnO-Al}_2\text{O}_3$ ) could decrease non-columbic loss and microbiologically induced corrosion of the Al-5% Zn anodes. Among these oxides, addition of nano  $\text{CeO}_2$  (ceria) has been considered more effective [11-12]. Anodic efficiency highly depend on the concentration of ceria in Al-5% Zn anodes. Aziz et. al. [13] and Rivera et. al. [14] studied the effect of higher concentration of  $\text{CeO}_2$  in Al-5% Zn alloys. They noted that when such material is exposed to the environment a barrier layer of  $\text{CeO}_2$  is formed on its surface and its anodic efficiency is decreased appreciably. The effect of particle size of ceria on the efficiency of Al-5% Zn anode is rarely studied.

In Pakistan, marine, oil and gas structures are being protected by ICCP despite the limitations of higher installation and maintenance cost along with stray current problems. Another issue concerned with SACP is the use of magnesium and zinc as sacrificial anodes which have less energy capabilities as compared to Al-5% Zn- anodes. Keeping in view the current research trend in the field of SACP and problems related marine, and oil and gas sectors in Pakistan an attempt is made to develop Al-Zn- $\text{CeO}_2$  sacrificial anode. The effect of particle size and concentration of  $\text{CeO}_2$  on the anodic efficiency of Al-5% Zn are investigated.

## 2. MATERIALS AND METHOD

To manufacture Al-5% Zn-ceria anode, Al and Zn ingot of 99% purity along with Merck-grade cerium nitrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) were used. The nano-ceria was synthesized using precipitation method, whereas Al-5% Zn anode was manufactured by traditional casting technique. The detailed procedure involved in the synthesis of nano-ceria and manufacturing of Al-5% Zn anode is described elsewhere [15]. The particle size and surface morphology of synthesized nano-ceria were determined using XRD (X-Ray Diffraction) and SEM (Scanning Electron Microscope) respectively. The FWHM (Full Width Half Maximum) was calculated from the XRD raw data and was used in Scherrer equation to determine the particle size of nano-ceria. Thereafter, nano-ceria particles were incorporated in the matrix of Al-5% Zn anode. Al-5% Zn-Ceria composite anode produced in electric resistance furnace by several steps such as (a) melting of Al-5% anode at  $750^\circ\text{C}$  (b) skimming off the slag (c) addition of ceria while maintaining the mixing conditions (d) pouring of molten mixture in cylindrical sand mold and finally machining of casted sample. Table 1 enlist the ID and different weight percentage of ceria in Al-5% Zn composite anode.

To evaluate the sacrificial tendency the variation in potential difference of Al-5% Zn-Ceria composite anode was determined when it was attached with mild steel cathode through closed circuit. The potential difference measured in close circuit will be referred hereinafter as close CCP. In CCP anode was mechanically fastened with mild steel cathode and immersed into 3% NaCl brine electrolyte bath at  $30 \pm 2^\circ\text{C}$ . The potential difference of anode and cathode was determined after interval of 24 hours. for period of 1 week using CCS (Copper/Copper Sulfate) reference electrode. The ratio between anode and cathode used was 1:5. In addition, the sacrificial tendency of anode was also determined by measuring the % weight

loss and CPR in CCP conditions. The detail of method used for percentage weight loss and CPR is reported [15]. The hardness of the anode was also determined by measuring the VHN (VickerHardness Number) at 1Kg<sub>f</sub> test load.

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization of Nano-Ceria

The XRD pattern of nano-ceria synthesized at different time intervals is shown in Fig. 1. XRD results indicates that the intensity of the ceria peaks were increased with increasing the precipitation time. The particle size calculated by FWHM value extracted from XRD patterns,

in Scherrer Equation. Particle size of ceria of 32, 47.6 and 82 nm were observed when precipitation time for 1, 2, and 3h, respectively. The increase in the particle size can be attributed with coalescence of particles by increasing the precipitation time.

To confirm the particle size and study the morphology of the ceria, particles were illuminated under SEM as shown in Fig. 2. SEM study revealed that ceria particles of rounded shape were synthesized when the precipitation time was set to 1h, whereas by increasing the precipitation time the agglomeration in the particles were noticed. The size of the ceria particles is almost in agreement with the size computed from Scherrer Equation.

TABLE 1. DESCRIPTION OF AL-5% ZN-CERIA COMPOSITE ANODE SAMPLES

Anode ID	Ceria Sample	Anode Composition	
		Ceria (%)	Al-5% Z (%)
AZ-1	-	0	100
AZ-2	N1	0.1	99.9
AZ-3		0.2	99.8
AZ-4		0.3	99.6
AZ-5	N2	0.1	99.9
AZ-6		0.2	99.8
AZ-7		0.3	99.6
AZ-8	N3	0.1	99.9
AZ-9		0.2	99.8
AZ-10		0.3	99.6

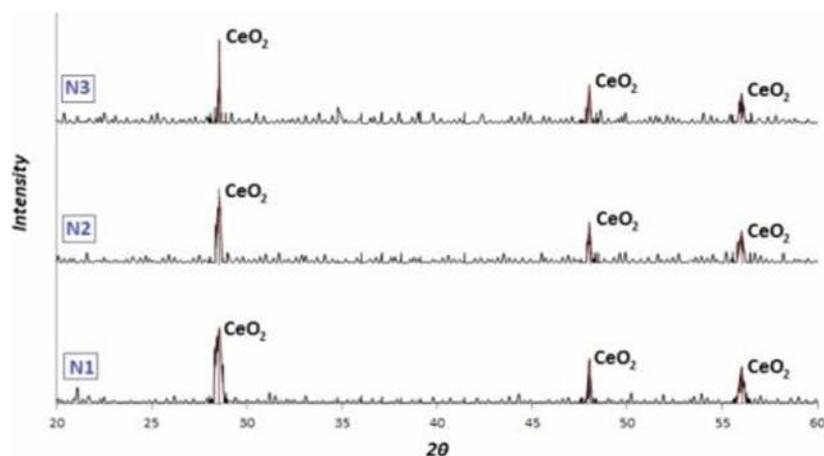


FIG. 1. XRD PATTERNS OF NANO CERIUM OXIDE N1, N2 AND N3

### 3.2 Sacrificial Tendency of Anodes

Sacrificial tendency of Al-5% Zn-ceria anodes was determined through monitoring the variation in emf for 168h in CCP system. Fig. 3 indicates that for period of 168h wide fluctuation in the emf of AZ1, AZ2, AZ3, AZ4 and AZ10 anodes, whereas emf of AZ4, AZ5, AZ7, AZ8 and AZ9 was remained quite stable. The anodes which do not maintain their emf below -0.9V would not compensate the loss of electrons of cathode efficiently, thus corrosion inhibition by the use of AZ1, AZ2, AZ3, AZ4, AZ8 and AZ10 could not be anticipated.

The performance of the anodes deduced from their emf values was further validated by monitoring the emf and CPR of the cathode. The variation in the emf of mild steel

cathode while coupling it with AZ1 to AZ10 anodes via CCP system is shown in Fig. 3. The utmost feature of the results shown in Fig. 4 is the significant contrast in the initial emf values of the cathode when it was coupled with AZ1, AZ3 and AZ10 hereinafter referred as Group-A anodes and AZ2, AZ4, AZ5, AZ6 and AZ9 hereinafter referred as Group-B anodes. It can be seen in Fig. 4 that the initial emf of the cathode with Group-A anodes about -0.6 V, while with Group-B anodes it was around -1.0 V. After 24h testing time the emf of the cathode either coupled with Group-A or Group-B anodes were reached to -0.8 V and maintained for additional 144 h with slight fluctuations. The initial emf value about -1.0 V suggest that an ideal immune condition was developed when the cathode was coupled with Group-B anodes.

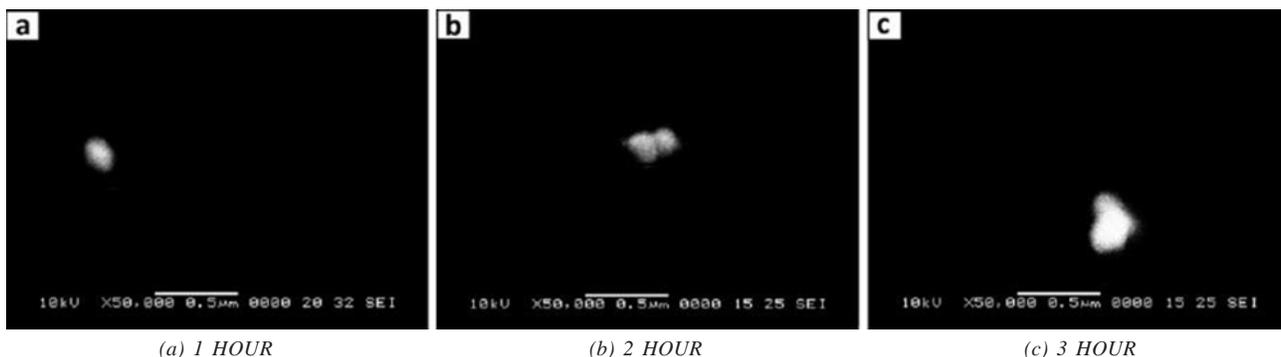


FIG. 2. NANO CERIA PARTICLE AFTER PRECIPITATION

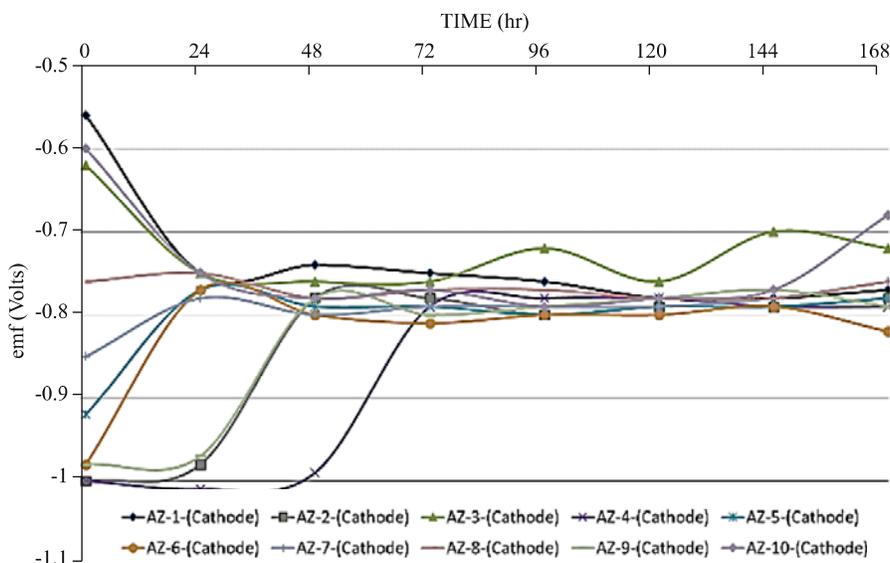


FIG. 3. TIME VS EMF CURVES OF MILD STEEL CATHODES

In contrast, the emf value of cathode developed with attachment of Group-A anodes infers that corrosion inhibiting environment was not established in initial test period. However, after 24 h the development of equivalent emf of cathode implies that Group-A and Group-B anodes behaved identically. In first glance the indistinguishable performance of Group-A and Group-B anodes after 24 h test period inferred from just emf values of cathode (Fig. 3) is quite discouraging and not in agreement with the speculated sacrificial behavior of anodes deduced from the emf of anode shown in Fig. 4.

In order to clarify the ambiguity in performance of anodes the emf of anode and cathode was plotted concurrently which is shown in Fig. 5. The important attribute displayed in Fig. 5 is the difference between the emf values of anode and cathode which hereinafter is referred as PD (Potential Difference). In fact, when engineering structures are protected from corrosion attack by SACP system then the rate of flow of electrons from anode to cathode depends on the PD value. For efficient SACP system it is compulsory that PD should be more than  $-0.1 \text{ V}_{(\text{min})}$ . The PD of AZ1 shown in Fig. 5 clearly explains that why poor

performance of Al-5% Zn anode for longer test time is widely acknowledged despite the fact that it exhibit quite high PD in early time of installation. Alike to AZ1 the poor sacrificial tendency of AZ3 and AZ8 anodes can be anticipated. In addition, Fig. 5 clearly demonstrates the poor performance of AZ2, AZ6, AZ7 and AZ10 anodes due to e wide fluctuation in the emf. Henceforth, the reliable and more efficient performance of only AZ4, AZ5 and AZ9 anodes can be speculated.

The CPR and CIE (Corrosion Inhibition Efficiency) of anodes were calculated with reference to CPR of Al-5% Zn anodes along with PD is shown in Fig. 6. It can be seen in Fig. 6 that the CPR of mild steel cathode was maximum (0.373) when PD of the coupling with Al-5% Zn anode was minimum ( $-0.03 \text{ V}$ ). In contrast, the CPR substantially reduced to  $0.008 \text{ mm/yr}$  when PD of coupling with Al-5% Zn-Ceria anodes was increased to  $-0.19 \pm 0.01 \text{ V}$ . Concomitantly, the CIE of AZ4, AZ5 and AZ9 anodes increased to 67, 76 and 100% respectively. The variation trend in the CIE shown in Fig. 6 clearly demonstrated the critical role of PD in governing the sacrificial efficiency of the anode.

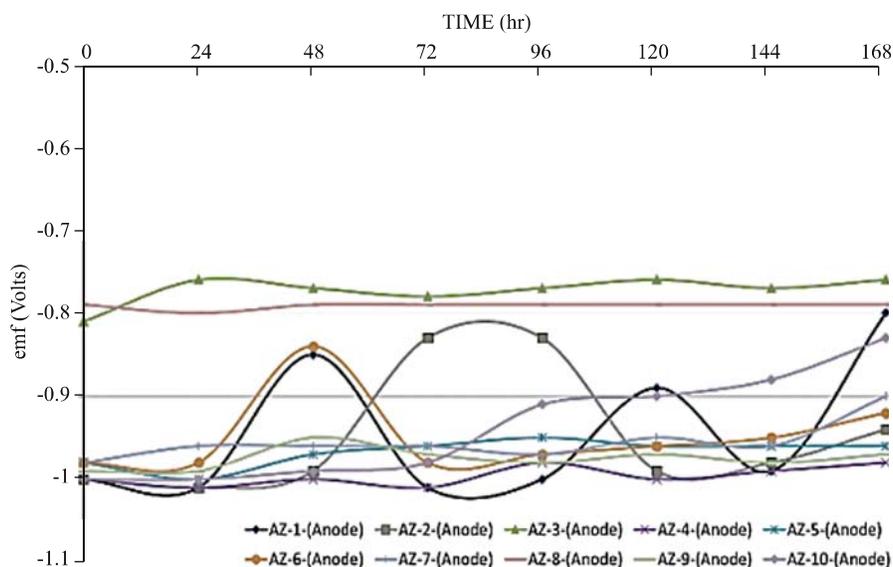


FIG. 4. TIME VS EMF CURVES OF AL-5% ZN-CERIA ANODES

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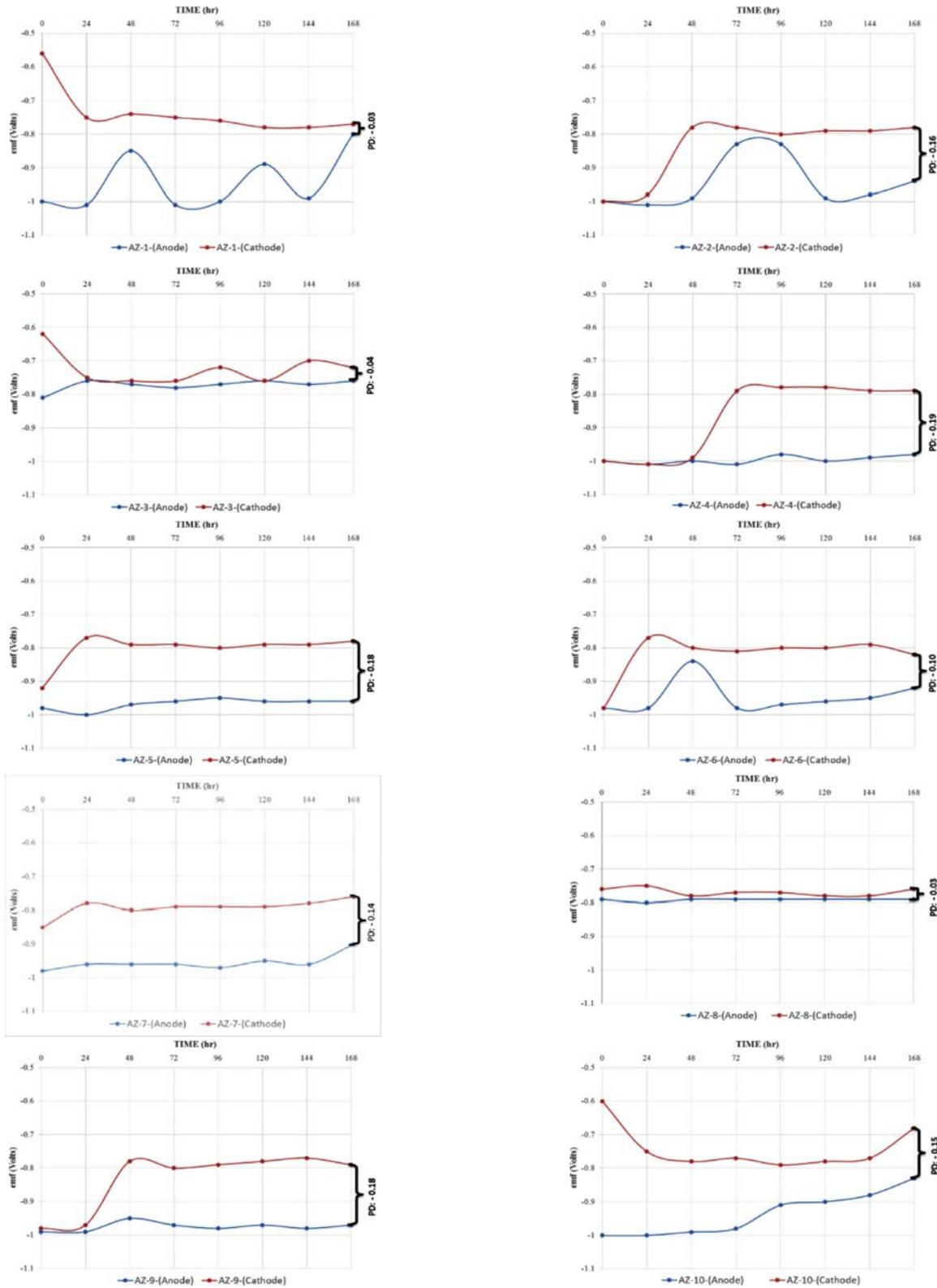


FIG. 5. TIME VS EMF CURVE BETWEEN EACH ANODE AND CATHODE

The appreciable improvements in the CIE of Al-5% Zn anode by compositing it with nano ceria needs to be explained. For this, the scientific reasoning on the basis of APS (Anode's Passivation Susceptibility) is used, since anodes exhibiting poor passivation susceptibility are alleged to have higher CIE. It is widely acknowledged in the literature that as and when the anodes passivate, their interaction with environment cuts, thus transfer of electrons from anode to cathode slows down and CIE of anodes reduces. From this point of view, it is anticipated that nano ceria would have played the part either in adjourning or interrupting anode passivation phenomenon of anode. Consequently time span of electrons flow from anode to cathode was extended by the presence of nano ceria particles. Interestingly, it is

noted that interruption in the Al- 5% Zn anode passivation is the function of size and concentration of the nano ceria.

Hardness result of Al-5% Zn anode as a function of ceria concentration is shown in Fig. 7, which demonstrates that hardness is also improved with addition of the ceria and improvement in the hardness is dependent on the size and concentration of nano ceria particles. Substantial increase in hardness with addition of ceria can be explained by correlating with physico-mechanical properties of ceria. Since ceria belongs to ceramic family, so by the addition of ceria increase in hardness of Al-5% Zn anode can be anticipated [16]. Moreover, the enhancement in the anode life can also be substantiated from the substantial improvement in the hardness.

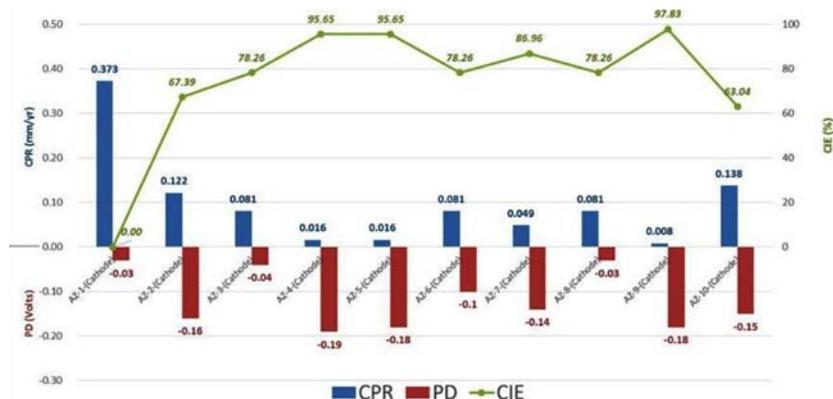


FIG. 6. RELATIONSHIP BETWEEN PD, CPR AND CIE

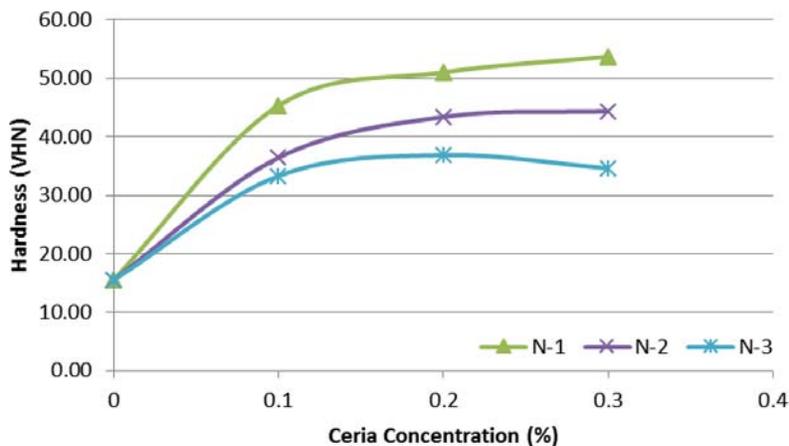


FIG. 7. ANODE HARDNESS AS A FUNCTION OF CERIA CONCENTRATION

## 4. CONCLUSIONS

Following conclusions were drawn:

- (i) By increasing the synthesis time the particle size of ceria was increased. For 1, 2, and 3 hour precipitation time ceria of 32, 47.6 and 82 nm was synthesized respectively.
- (ii) With addition of ceria in Al-5% Zn anode the sacrificial anodic efficiency improved significantly. The reliable and more efficient performance of AZ4, AZ5 and AZ9 anodes was noted based on PD, CIE and CPR.
- (iii) Addition of ceria also enhanced the hardness of the anodes and it was speculated that due to increase in the hardness the life of the anode may also increase.

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