

Effect of environmentally friendly additives on Zn-Mn alloys morphology and structure

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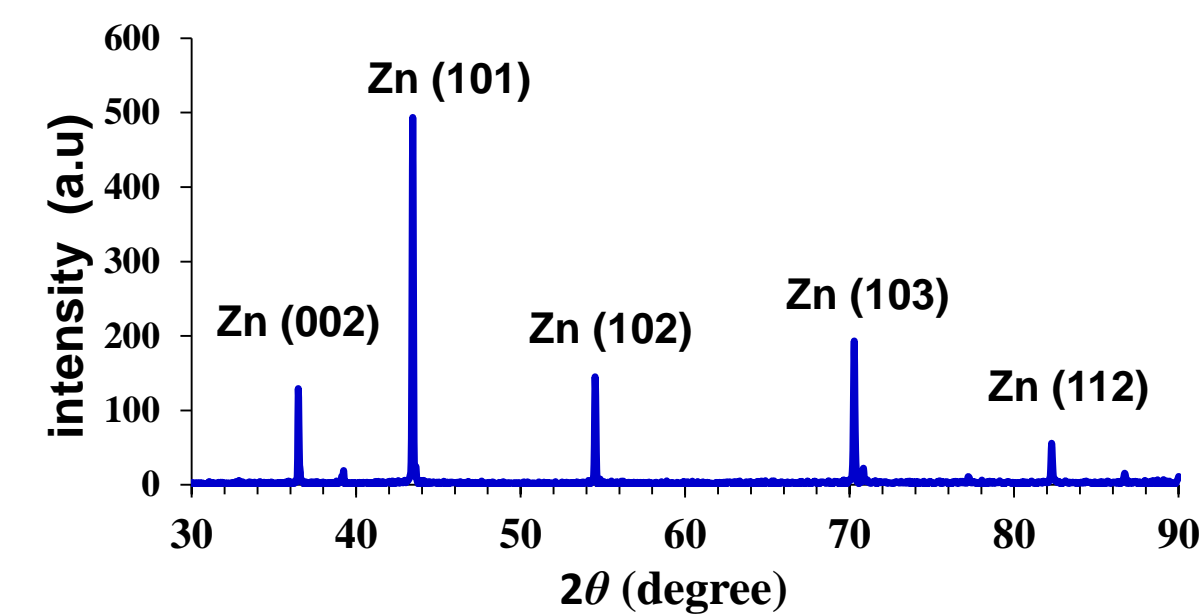
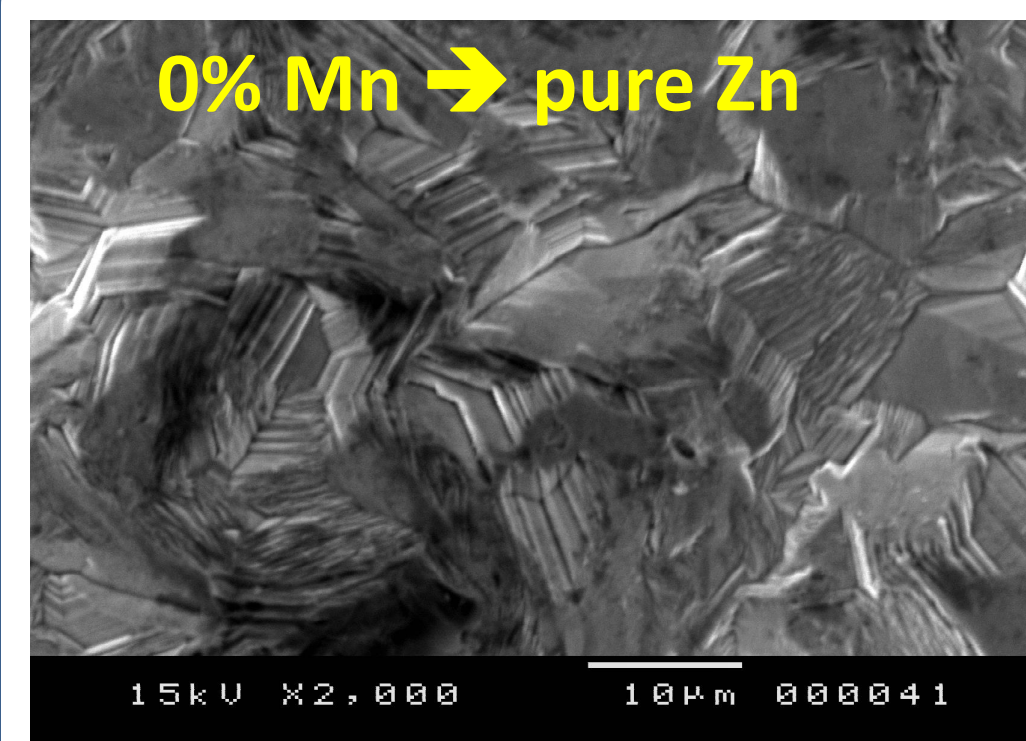
Abstract

Pure Zn coating commonly used for the protection of steel is not sufficient in some industrial applications due to its high dissolution rate. There is a growing interest in Zn-Mn coatings owing to the highest corrosion resistance compared to that of pure zinc coatings. In this work, a novel additive based on Octylphenylpoly(ethyleneglycol)₁₀ and 3-hydroxybenzaldehyde 3-HBA was investigated in Zn-Mn electrodeposition on steel from chloride bath. These additives inhibit Zn deposition in favor to that of Mn owing to their adsorption on the surface cathode. Thus, Zn-Mn alloys were successfully electrodeposited with suitable properties. The Mn content reaches around 20%. SEM data reveal that Zn-Mn exhibits fine morphology.

Morphological and Structural properties of Zn-Mn alloys

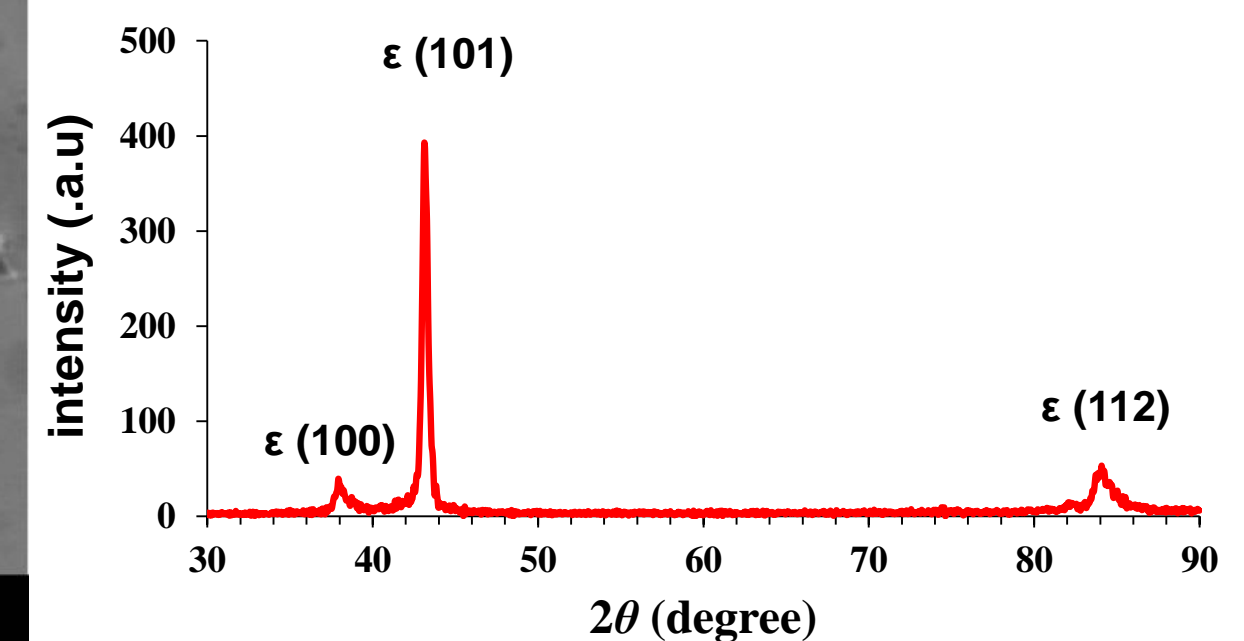
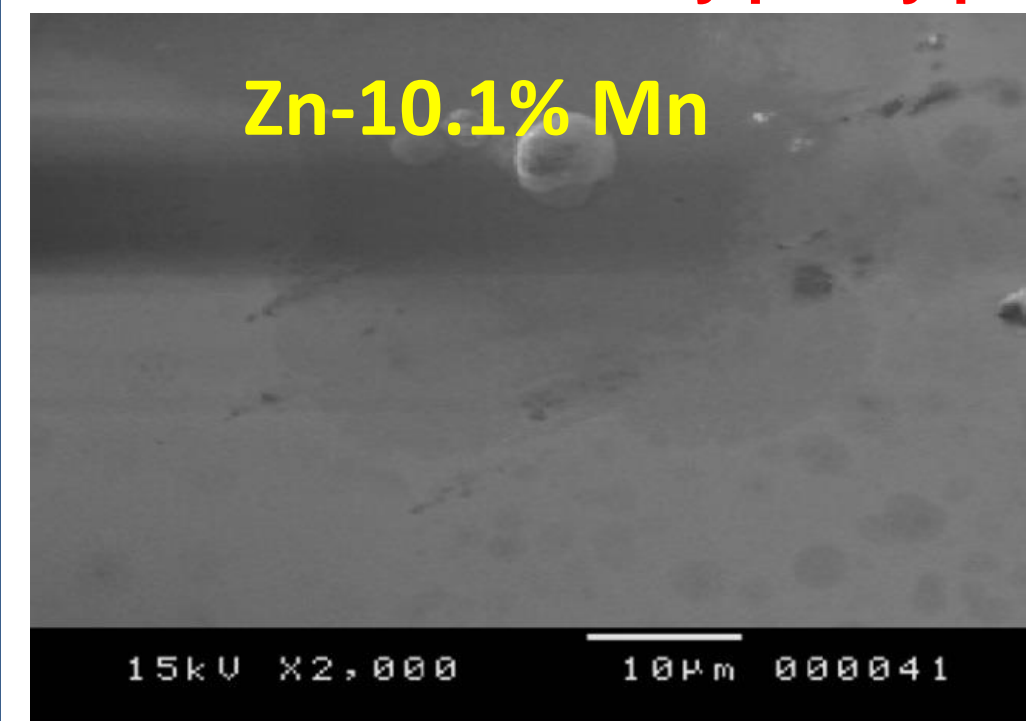
$j = 30 \text{ mA/cm}^2$

Without additives



Zn crystals grow under different crystallographic orientations

With additives Octylphenylpoly(ethyleneglycol)₁₀ + 3-HBA



Only ϵ -Zn-Mn phase

Smooth Zn-Mn alloys

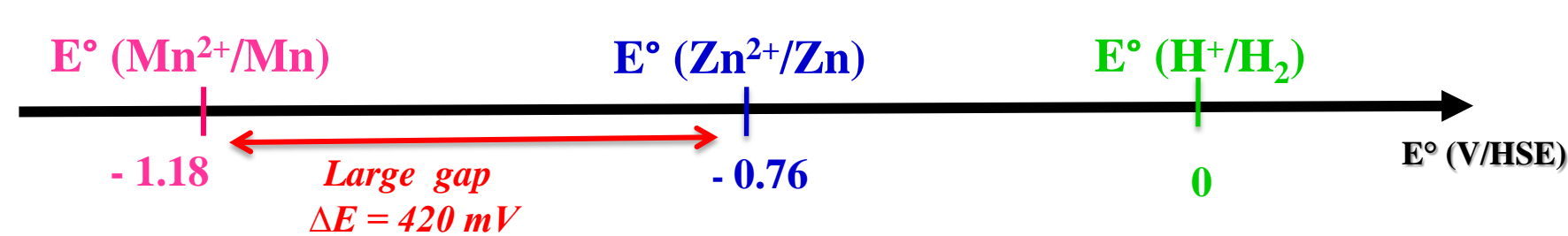
When additives are added into electrolytic bath

➤ SEM observation → : transition from platelet grains of pure Zn to finer grains

➤ XRD patterns → monophasic alloy preferential orientation along specific direction due to different rates of growth of different faces of the crystal

Major problems of Zn-Mn co-deposition

1. Large gap between Zn and Mn deposition potentials :



2. Hydrogen evolution reaction inhibits Mn co-deposition with Zn

3. Mn-rich alloys require high current densities leading to powdery alloys

Use of **complexing agent specific for Zn²⁺ reduction** to ensure Zn-Mn co-deposition. Stringent environmental concerns have restricted the complexing agent due to **serious problems related to wastewater treatment**.

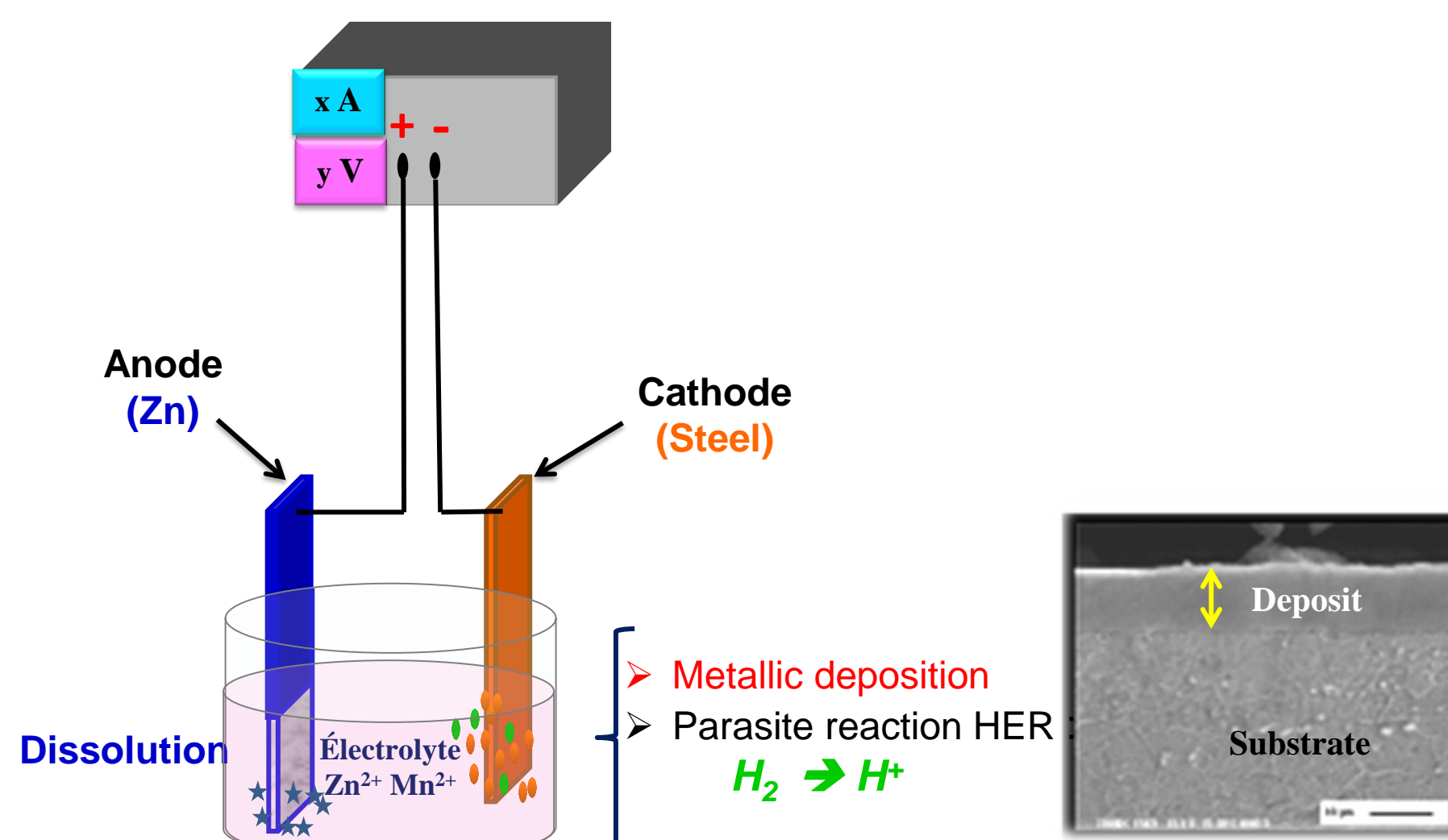
Experimental details

Experiments were carried out from an acidic chloride bath S_{Zn-Mn}

Chemical constituent	KCl	H ₃ BO ₃	ZnCl ₂	MnCl ₂
Concentration (mol/l)	3.2	0.4	0.4	0.4

Bulk electrolysis

Digital dc power supply



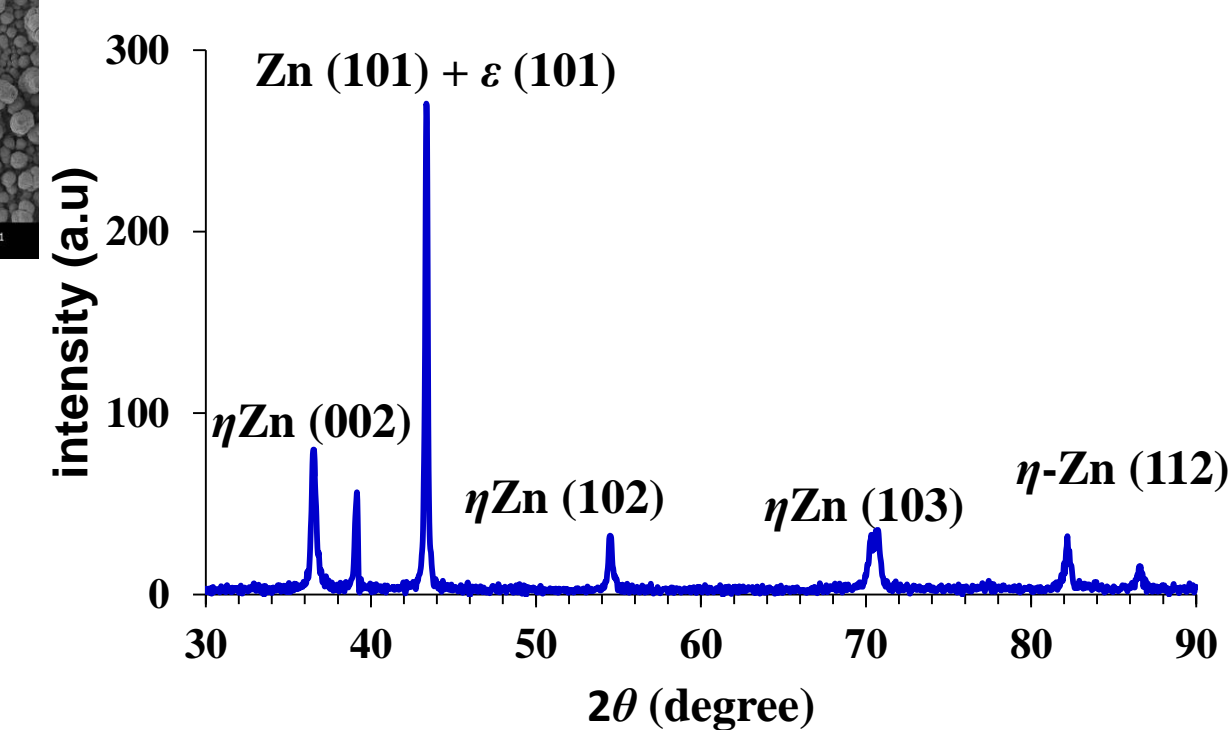
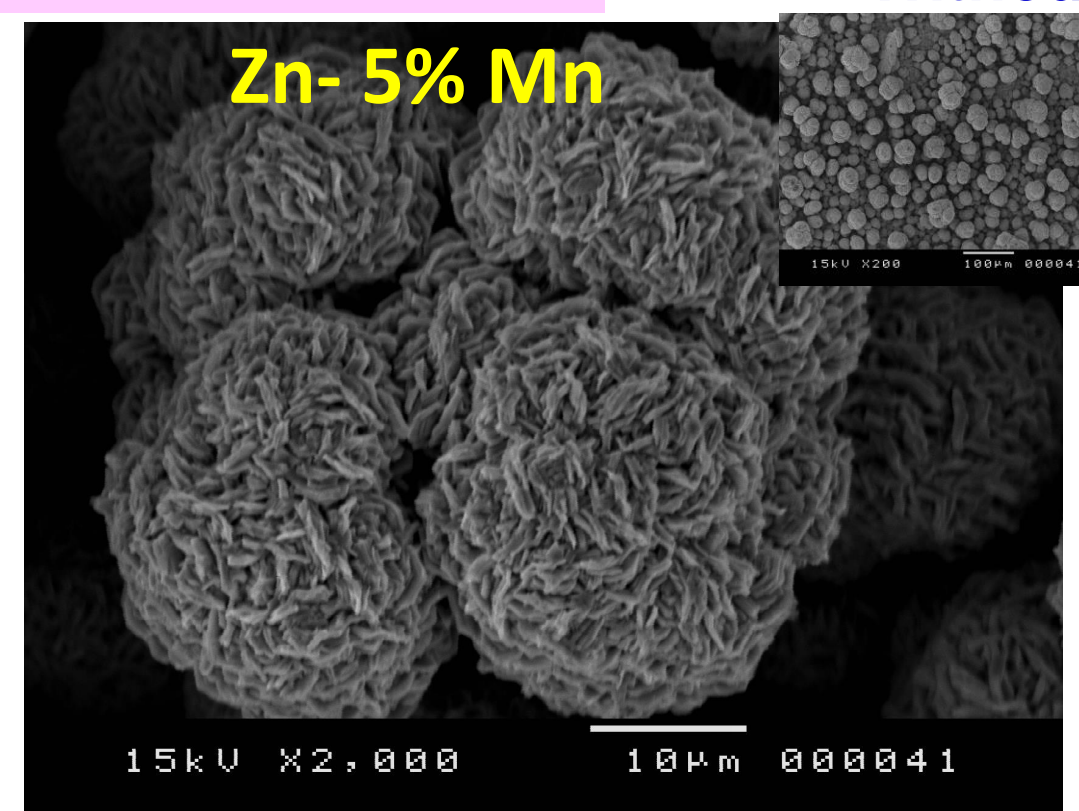
➤ Galvanostatic experiments were carried out from the working electrolyte S_{Zn-Mn} containing or not **Octylphenylpoly(ethyleneglycol)₁₀ + 3-HBA**

➤ Two applied Current densities :

1. $j = 30 \text{ mA/cm}^2$
2. $j = 75 \text{ mA/cm}^2$

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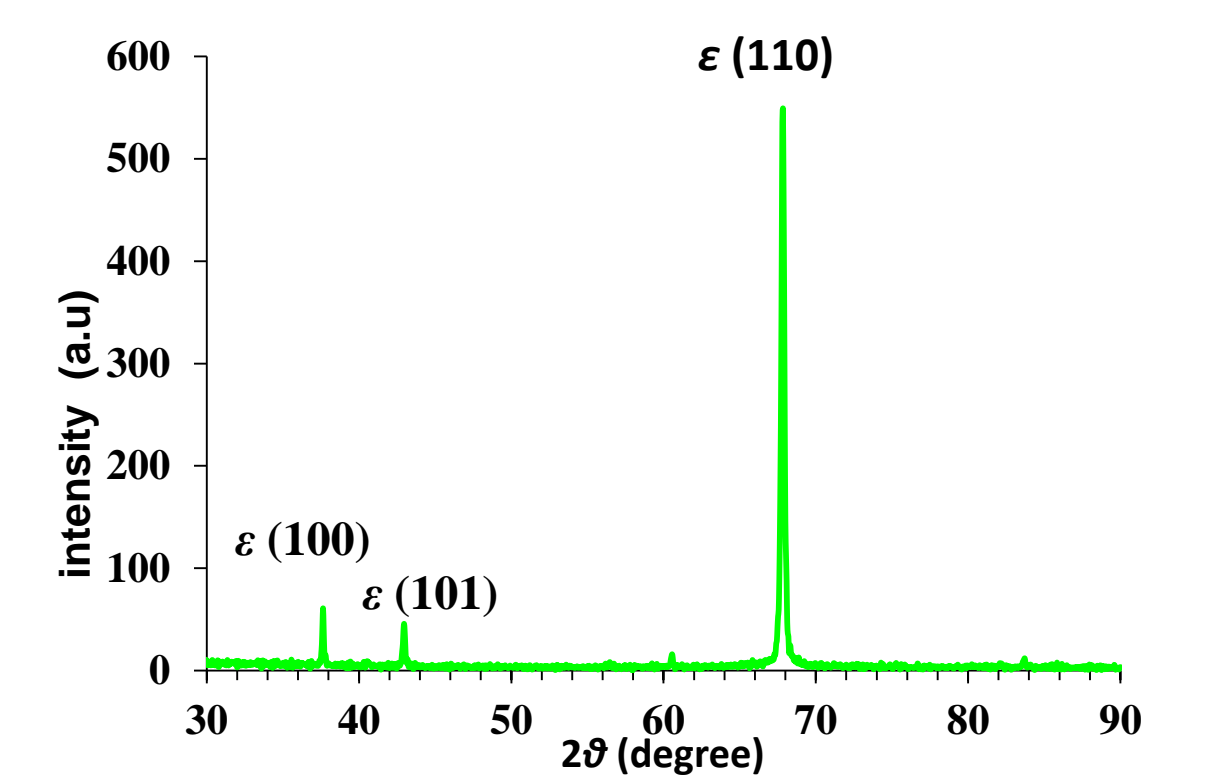
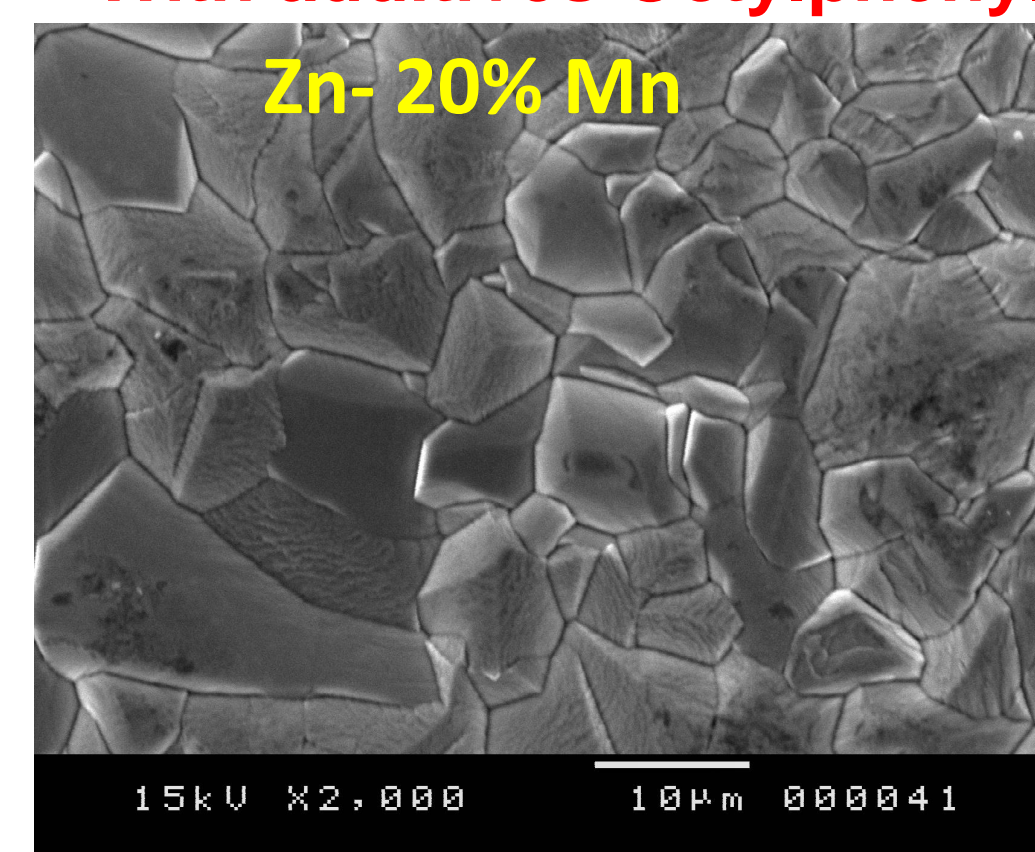
Without additives



When j increases : → Zn-Mn is dendritic : attesting that the growth process is under diffusion control

Zn-5% Mn is bi-phasic alloy

With additives Octylphenylpoly(ethyleneglycol)₁₀ + 3-HBA



Mn-rich alloys: → Large grains with non-uniform size and shape

At high Mn content → Zn-Mn alloy is monophasic with preferred orientation along (110)

Conclusion

Octylphenylpoly(ethyleneglycol)₁₀ and 3-HBA :

- ✓ are turned out to be **efficient potential additives** to enable an easier Mn incorporation into Zn matrix → Mn-rich alloys are obtained
- ✓ alters Zn-Mn alloy morphology with a preferred orientation.
- All modifications in Zn-Mn coatings suggest a change in the nucleation and growth of crystals in presence of additives. This occurrence is associated with **the adsorption of organic molecules on the cathode surface**.