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Development and industrial application of novel non-cr passivity for electrolytic manganese

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Research on mechanism of one-step preparation of intelligent self-healing protective coating on Mn surface

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1. Introduction

Mn, as an important raw material, is readily oxidized in air

Passivation method:
chromate treatment
- **Good passivation behaviors**
- **Pollution**

Phosphate membrane: simple & anti-corrosion

Developing direction:
chromate free passivity

P-based passivity of Mn

Current situation:
Bad passivation

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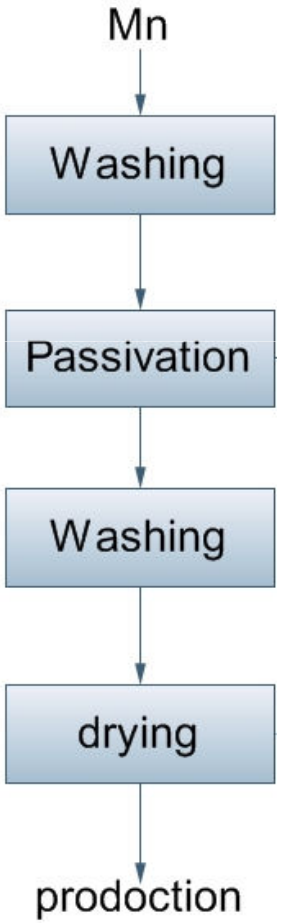
2. Membrane preparation

2.1 Passivation method (H_3PO_4 as passivity):



Schema of treatment process

Appearances of Mn treated by chromate (Cr-Mn) (left) and H_3PO_4 (P-Mn) (right)

Requirement of manganese product

- Bright appearance
- Acceptable Impurity content

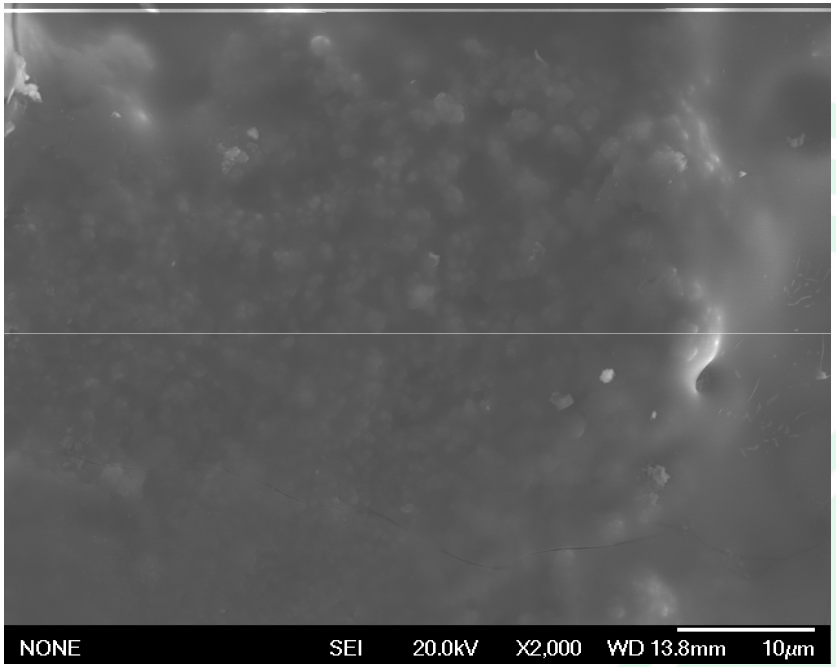
2. Membrane preparation

2.2 Analysis of P-based membrane:

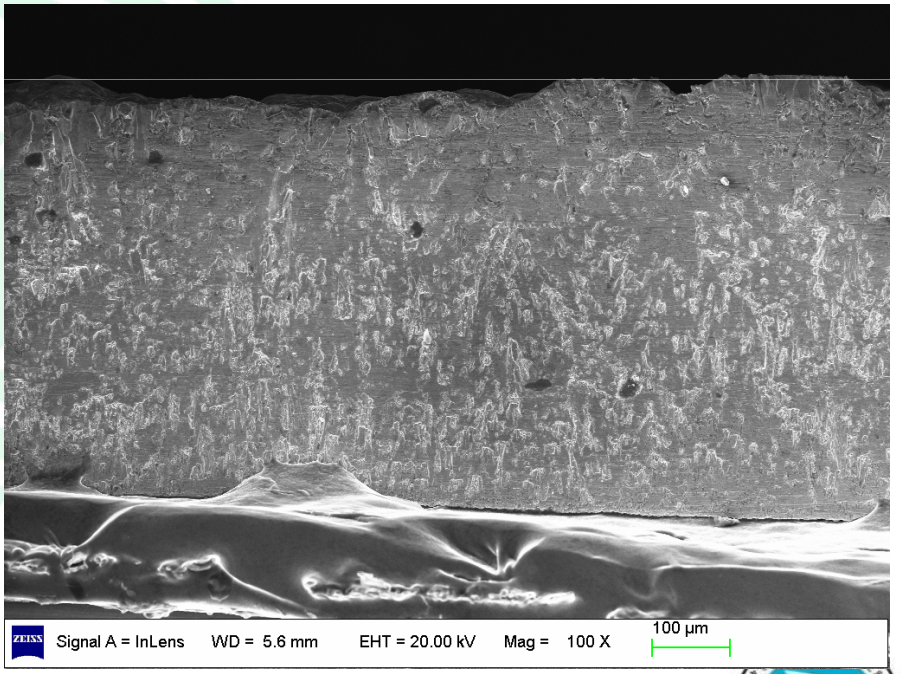
$Mn_3(PO_4)_2$

Chemical content of coating

Element	Mn	P	O
Content（%）	23.02	16.22	60.76



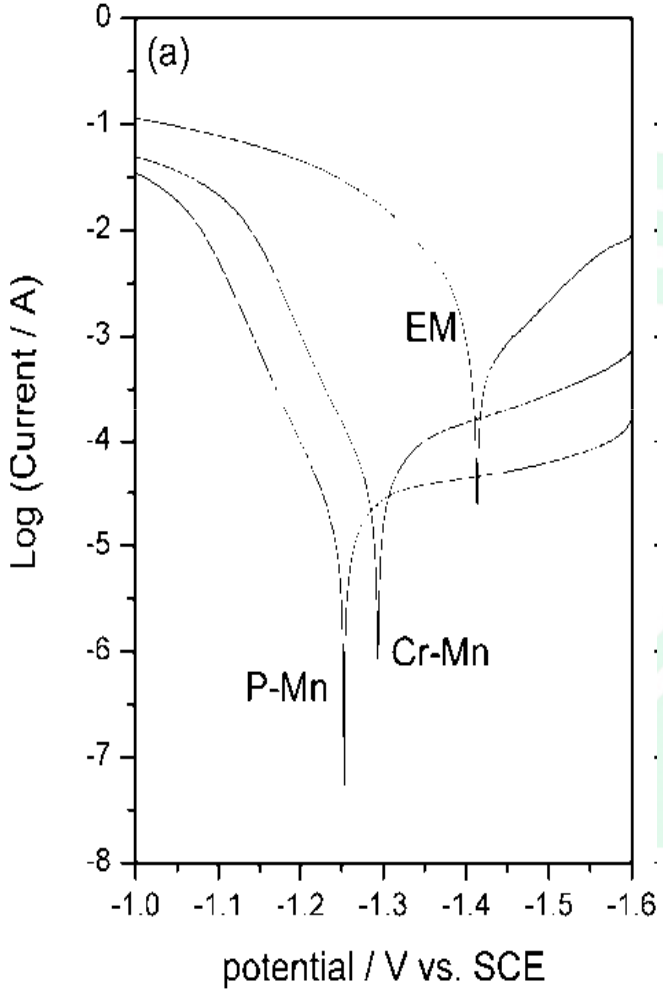
SEM image of P-Mn



SEM cross-section image of P-Mn

2. Membrane preparation

2.3 Corrsion resistance :



Tafel curve of Mn treated by different methods in 3.5% NaCl solution

High current density implys high corrosion rate

in 3.5% NaCl solution

Sample	E_{corr} (V)	I_{corr} (μA/cm$_2$)
EM	-1.41	321
Cr-Mn	-1.29	12.9
P-Mn	-1.25	5.3

Corrosion resistance: P-Mn>Cr-Mn>EM

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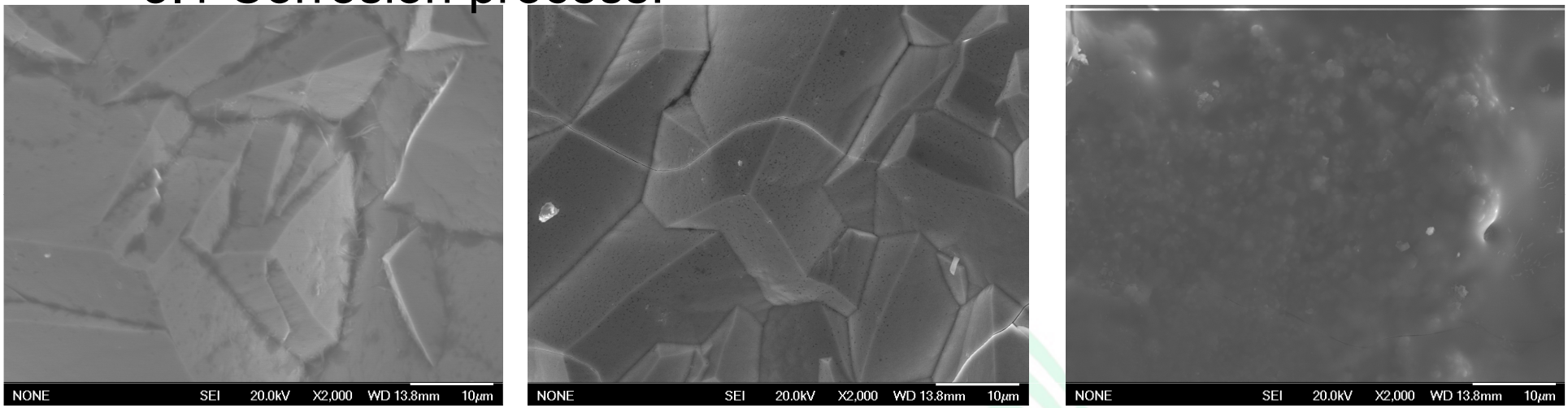
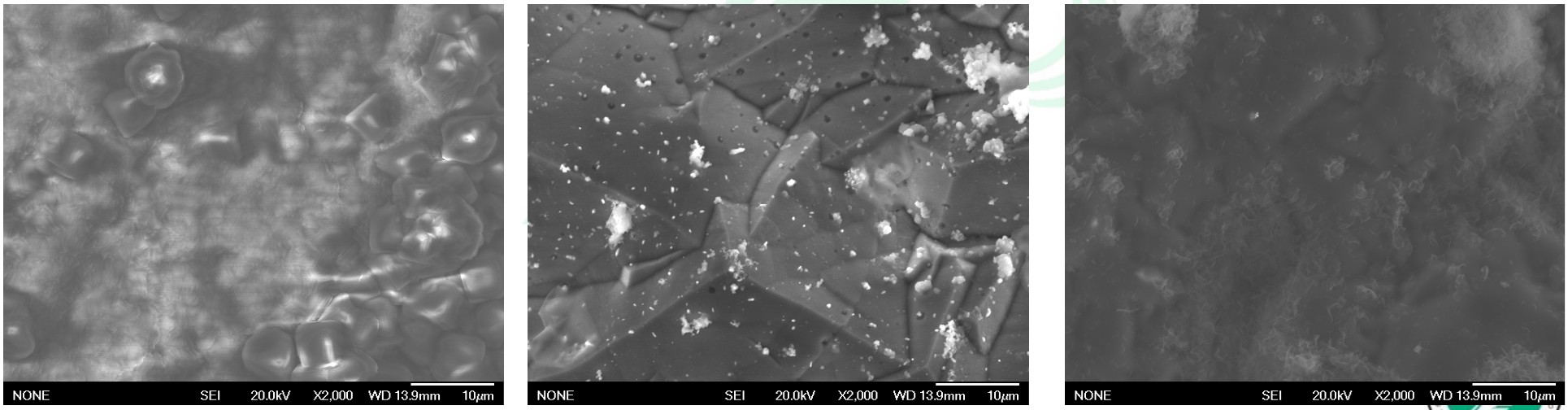
3. Corrosion of P-based membrane

3.1 Corrosion process:



SEM image of Mn (left), Cr-Mn (centre) and P-Mn (right) before immersion in 3.5% NaCl solution

24h corrosion



SEM image of Mn (left), Cr-Mn (centre) and P-Mn (right) after immersion for 24 h

3. Corrosion of P-based membrane

Compositional variation of membrane

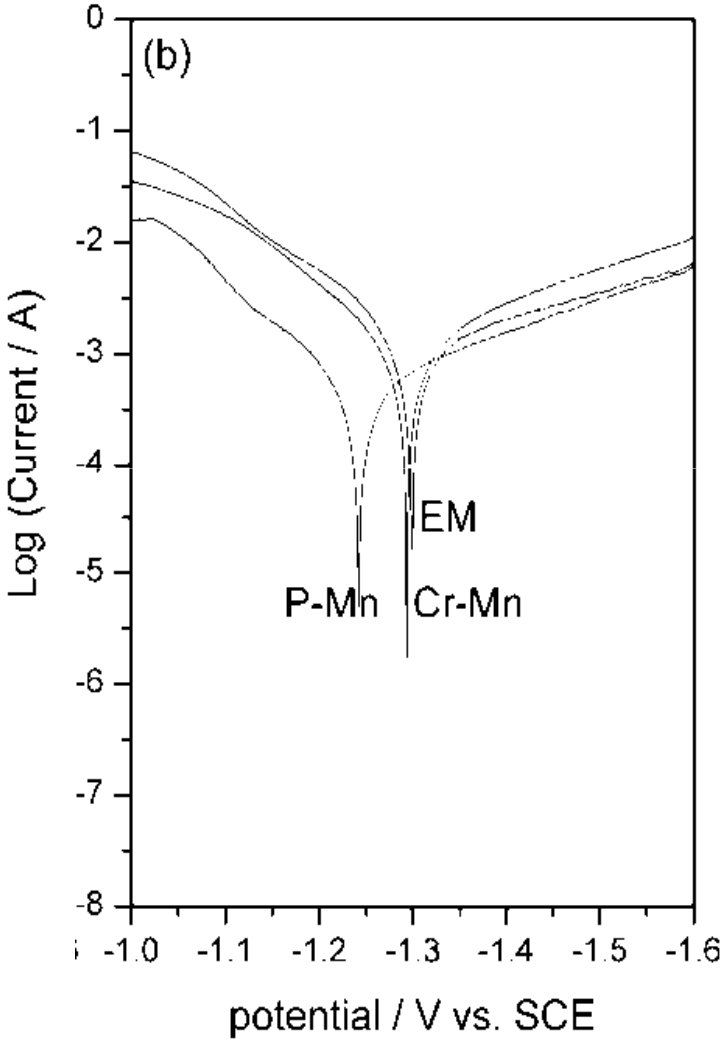
		Mn	TO*	Cr	P	RO**	O: Mn***
Mn	Before	84.93	0	-	-	0	0
	After	23.29	54.22	-	-	54.22	2.38
Cr-Mn	Before	94.48	0	0.12	-	0	0
	After	60.72	19.10	0.10			0.31
P-Mn	Before	23.02	60.76	-	16.22	~0	~0
	After	53.30	31.49	-	9.40	~0	~0

MnO_2

Corrsoion inhibition

*: TO: total O
**: RO: remaining O, RO= TO- (P×4)
***: O:Mn=RO÷Mn

3. Corrosion of P-based membrane



Tafel curve of Mn treated by different methods in 3.5% NaCl solution after 24h immersion

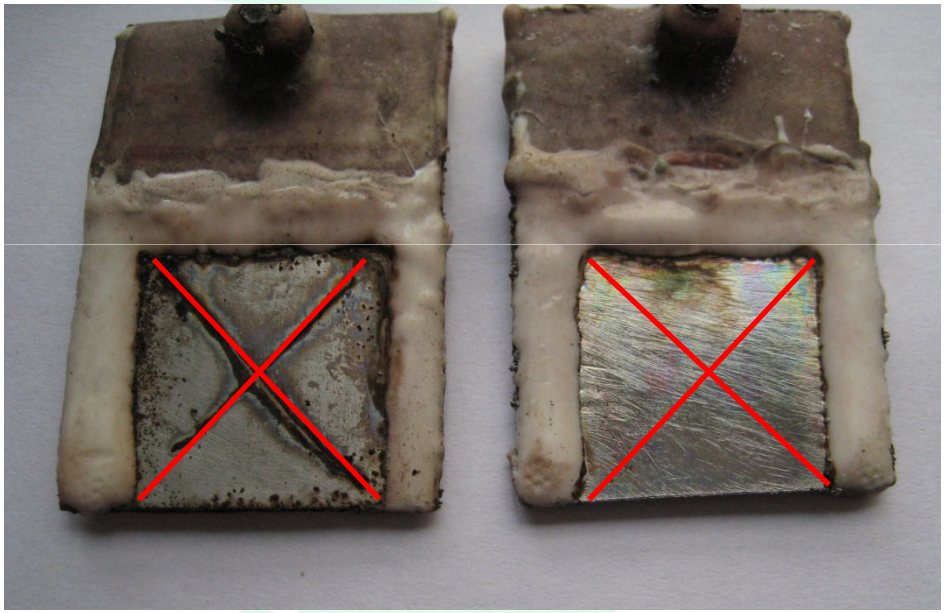
Parameter of Tafel curve in 3.5% NaCl solution after 24h immersion

Sample	E_{corr} (V)	I_{corr} (μA/cm$_2$)
EM	-1.29	3130
Cr-Mn	-1.29	284
P-Mn	-1.25	140

Retention of Corrosion resistance: P-Mn>Cr-Mn>EM

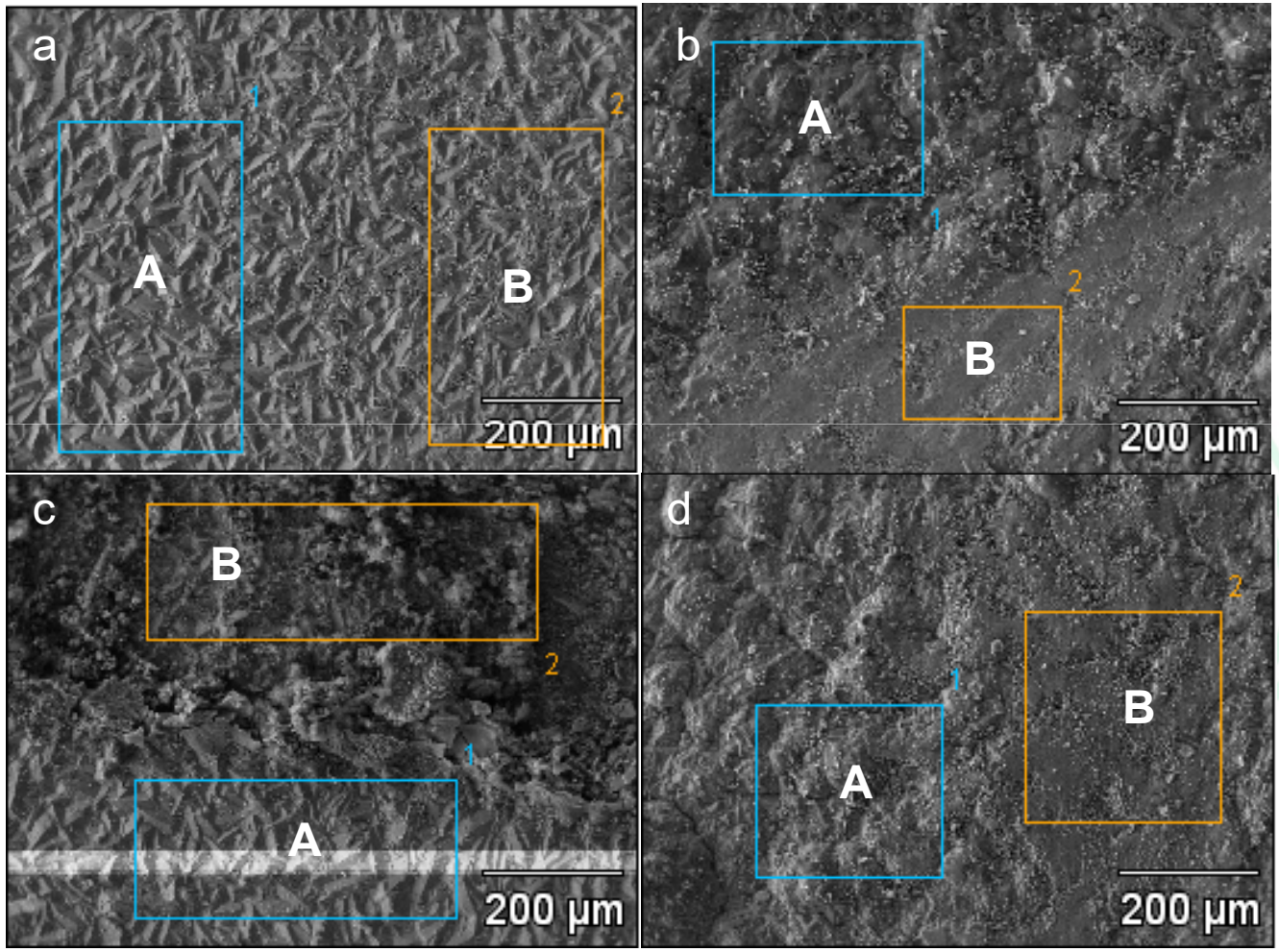
3. Corrosion of P-based membrane

3.2 : self-healing capability test



Photos of Cr-Mn and P-Mn with damaged membrance after immersion in 3.5% NaCl solution for 24 h

3. Corrosion of P-based membrane



SEM image: before immersion: Cr-Mn(a) and P-Mn(b) with damaged membrane;
after immerison in 3.5% NaCl solution: Cr-Mn(c) and P-Mn(d) with damaged membrane

3. Corrosion of P-based membrane

Compositional variation of membrane

	Immersion time (h)	Membrane statue	Mn	TO*	Cr	P	RO**	O：Mn***
Cr-Mn	Before	Zone A	89.4	0.7	0.36	-	0.7	0.007
		Zone B	100	-	-			
Part with intact membrane	after	Zone A	55.3	18.0	0.2	-	18.0	0.325
Part with damaged membrane		Zone B	33.2	64.4	-	-	64.4	1.94
P-Mn	Before	Zone A	27.5	57.6	-	14.9	~0	~0
		Zone B	86.4					
	after	Zone A	58.3	36.1	-	5.6	13.7	0.234
		Zone B	39.7	38.4	-	1.28	33.28	0.838

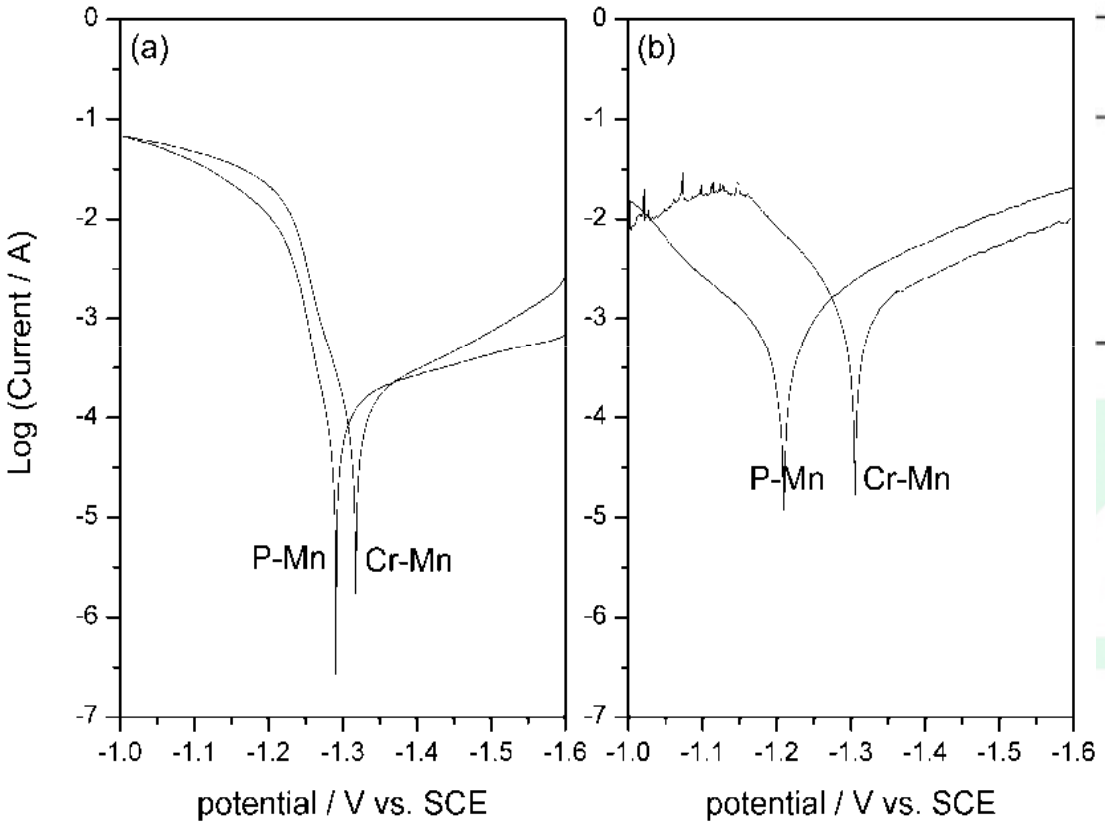
Most of Mn are oxidized.

Degree of oxidation is much lower

*: TO: total O
**: RO: remaining O, RO= TO- (P×4)
***: O:Mn=RO÷Mn

Self-healing capability: P-Mn>Cr-Mn

3. Corrosion of P-based membrane



Tafel curve of samples with damaged membrane in 3.5% NaCl solution for 24 h

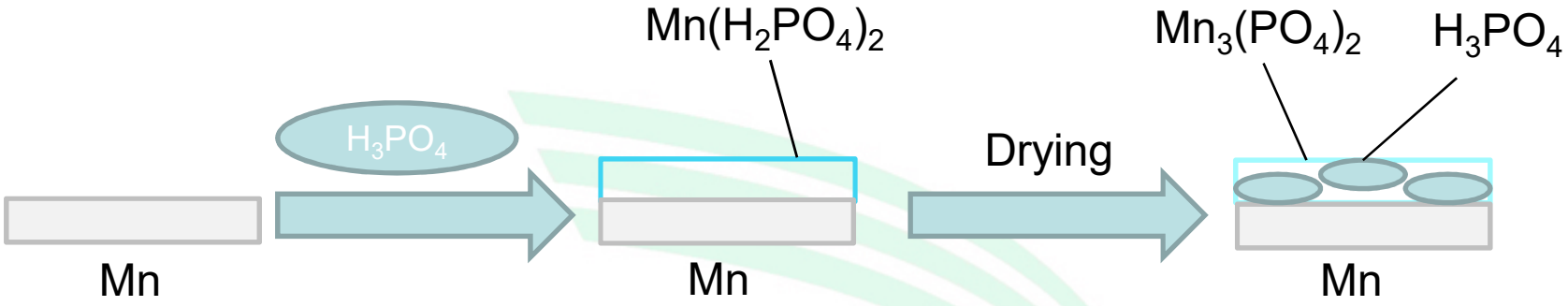
Parameter of Tafel curve in 3.5% NaCl solution

Sample	Immersion time (h)	E_{corr} (V)	I_{corr} (μA/cm^2)
P-Mn	0	-1.28	34
	24	-1.21	250
Cr-Mn	0	-1.32	38.5
	24	-1.31	413.3

P-Mn has better retention of corrosion inhibition capability when its membrane damaged.

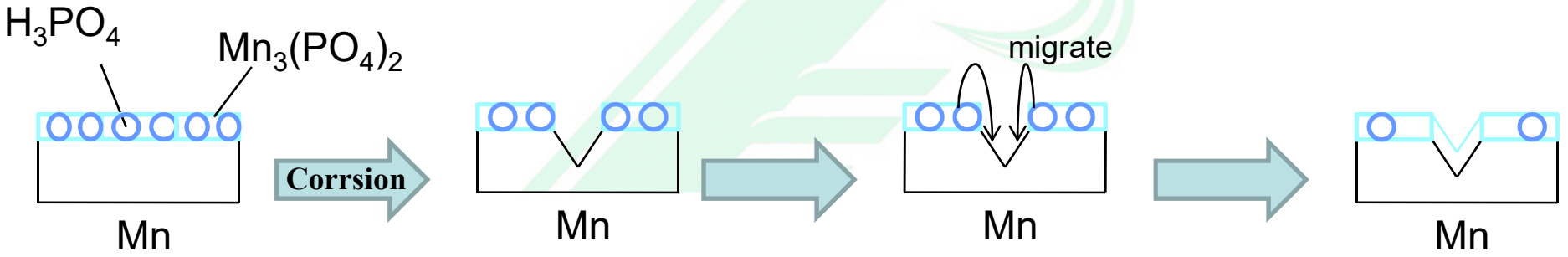
3. Corrosion of P-based membrane

3.3 mechanism:



Schema of P-based membrane formation

$$Mn+H_3PO_4 \rightarrow Mn(H_2PO_4)_2+H_2\uparrow$$
$$3Mn(H_2PO_4)_2 \rightarrow Mn_3(PO_4)_2\downarrow+4H_3PO_4$$



Schema of anti-corrsion process

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4. Novel passivity in industrial application

P-based coating on Mn surface has good anti-corrosion and self-healing capability. However, it's harmful for quality of Mn with high P content. A novel passivity with lower P content have been invited, and used in Mn industrial production.

4. Novel passivity in industrial application

4.1 Industrial application of novel passivity

Impurity content

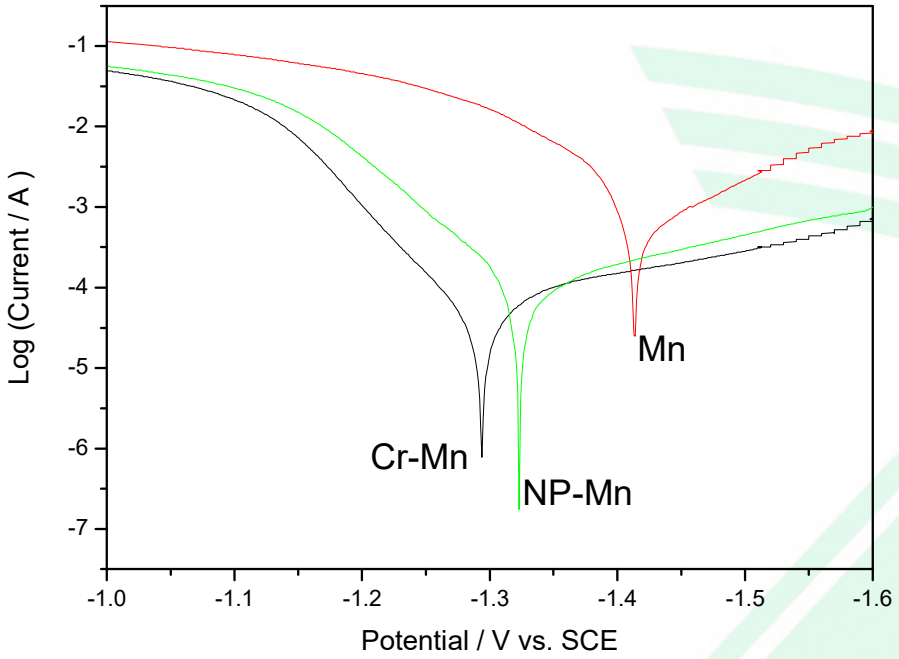
	Our product	Standards
C	0.0064%	≤0.02%
P	0.0032%	≤0.005%
S	0.020%	≤0.03%

Accord with production standards YB/T051-93, which used current.

Photos of Mn treated by novel P-based passivity in industrial production in XES. LTD.

4. Novel passivity in industrial application

4.2 Anti-corrosion capability:



Tafel curve of Mn treated by different methods in 3.5% NaCl solution

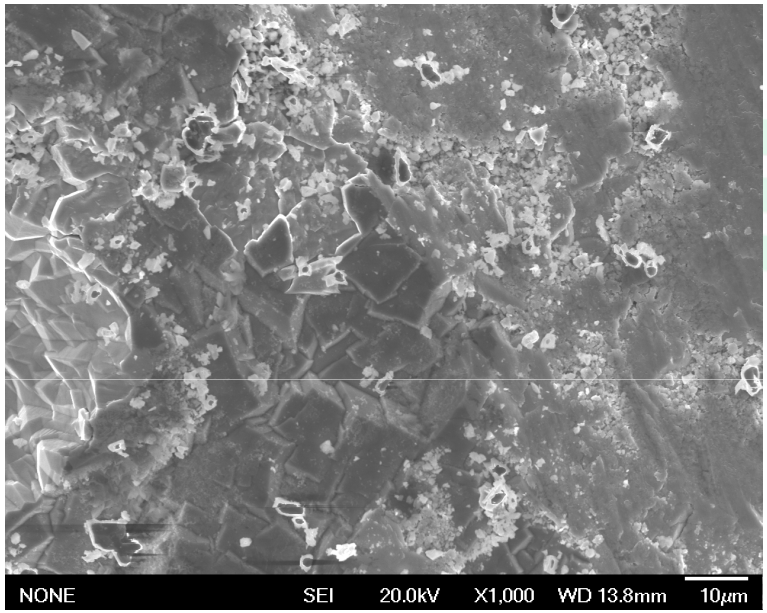
Parameter of Tafel curve in 3.5% NaCl solution

	Cr-Mn	NP-Mn	Mn
E_{corr} (V)	-1.29	1.34	-1.41
i_{corr} ($\mu A/cm^2$)	12.9	40.7	3130

Even though corrosion current density of NP-Mn is higher than Cr-Mn in corrosion media , it just covers ca. 1/75 of Mn. It implies novel passivity we developed has a good passivation capability for manganese.

4. Novel passivity in industrial application

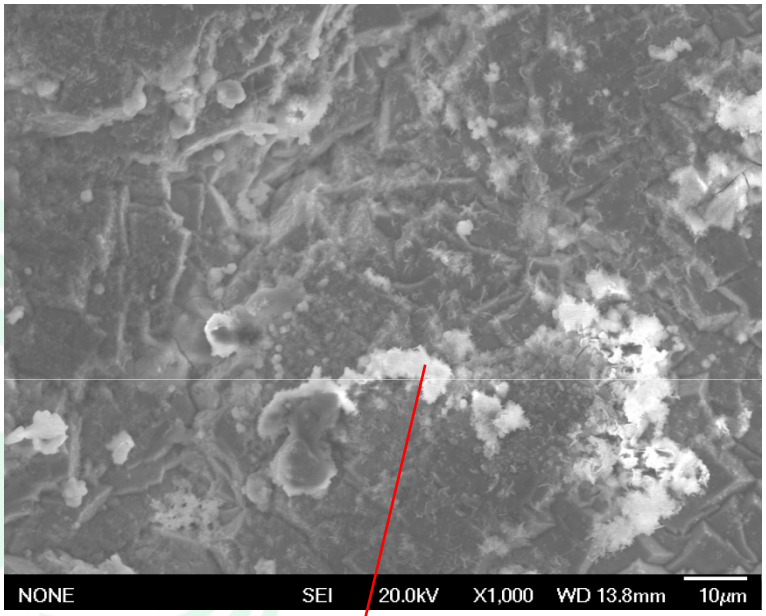
4.3 analysis of corrosion product:



SEM image of NP-Mn

24h

immersion



SEM image of NP-Mn after immersion in 3.5% NaCl solution for 24 h

Cr-Mn:
O:Mn=0.325

Compositional variatio

	TO	P	Mn	RO	O:Mn
before	7.26	0.57	73.47	4.78	0.065
after	26.42	0.77	47.08	23.34	0.50

Good anti-corrosion behavior than pure Mn in corrosion media

4. Novel passivity in industrial application

4.4 Product of Mn in industrial production

Photos of Mn treated by chromate (left) and novel P-based passivity (right) in industrial production (preserve at arbitrary temperature for Ca. 3 months)

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4. Conlusions

1. According to deficiency of current chromate and non-Cr passivity, H_3PO_4 is used as a main passivity in our research. It's found that phosphate membrane formed on Mn surface had a great anti-corrosion capability. Results from EDS showed that its main component is $Mn_3(PO_4)_2$.

2. Experiment results show that phosphate membrane have better self-healing capabilities.

3. Results of industrial application of novel P-base passivity showed that Mn which treaded by novel P-based passivity had a bright appearance and good anti-corrsion capability. Its impurity content accorded with production standards YB/T051-93.

Thank You for your attention!

And welcome to China!