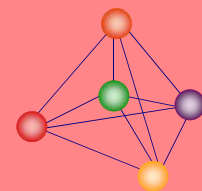




# Electrodeposition of Tin using Supercritical Carbon Dioxide Emulsion

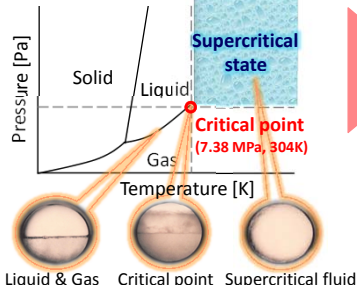
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## Introduction

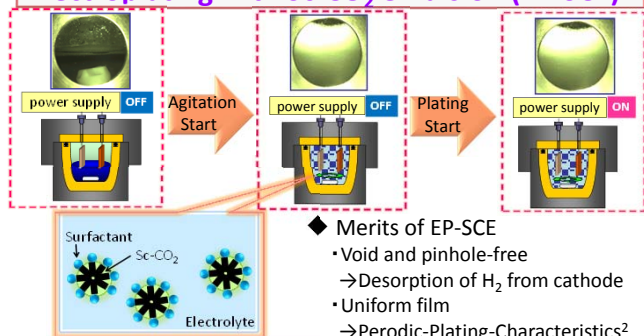
### Supercritical carbon dioxide (Sc-CO<sub>2</sub>)



- ◆ Feature of Sc-CO<sub>2</sub>
  - low viscosity (high diffusivity)
  - high density
  - miscibility with H<sub>2</sub>

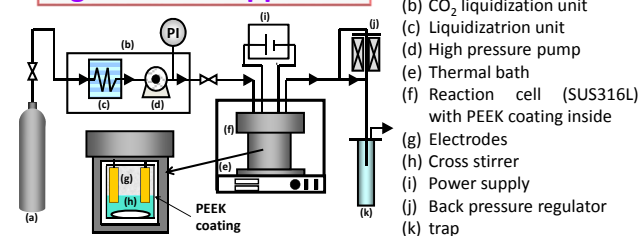
To conduct electrochemical reactions,  
Surfactant is added to form Sc-CO<sub>2</sub>  
emulsified electrolyte

### Electroplating with Sc-CO<sub>2</sub> emulsion (EP-SCE)<sup>1</sup>



## Experimental

### High Pressure apparatus



### Materials

#### Electrodes

- cathode : Ni
- anode : Sn

#### Electrolyte

- SnCl<sub>2</sub> · 2H<sub>2</sub>O (0.22 mol/L)
- HOC(COONH<sub>4</sub>)(CH<sub>2</sub>COONH<sub>4</sub>)<sub>2</sub> (0.31 mol/L)
- HCl (0.015 mol/L)
- CO<sub>2</sub> (20 vol.%)

#### Surfactant (EP-SCE)

- polyoxyethylene lauryl ether (C<sub>12</sub>H<sub>25</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>15</sub>OH)
- 0.2 vol.% with electrolyte

### Conditions

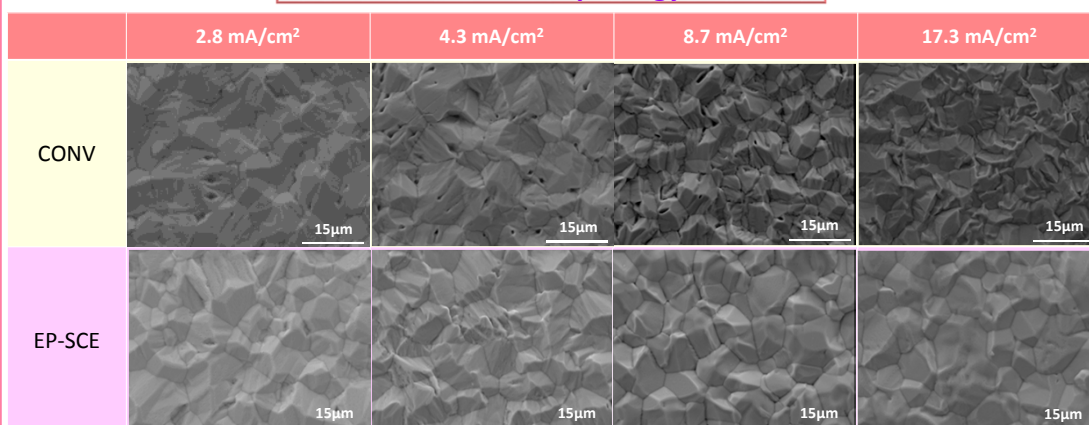
- Pressure : atmosphere (CONV)  
15 MPa (EP-SCE)
  - Temperature : 343 K
  - Current density : 2.8, 4.3, 8.7, 17.3 mA/cm<sup>2</sup>
  - Plating time : 92, 60, 30, 15 min (respectively)
- Theoretical film thickness, about 13 μm**

### Pretratment

- Ethanol for 5 min
- HCl for 5 min

## Results and discussion

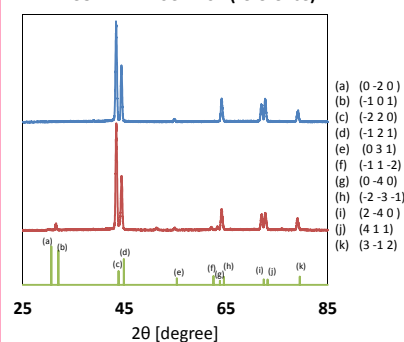
### Surface morphology



Eliminate void in the film by EP-SCE → Promoted desorption of H<sub>2</sub>

### XRD

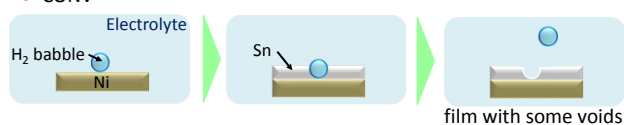
Electroplating : 17.3 mA/cm<sup>2</sup> and 15 min  
— CONV — EP-SCE — Sn (reference)



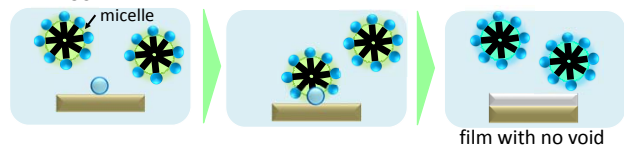
By scherrer's equation,  
grain size is about 30 nm for both cases.

### Mechanism of electrodeposit by CONV and EP-SCE

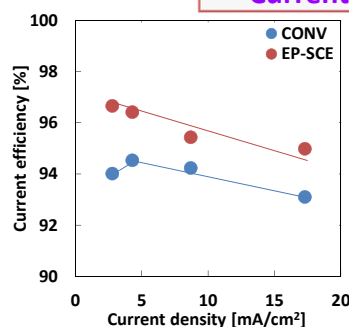
#### • CONV



#### • EP-SCE



### Current efficiency



• Current efficiency of EP-SCE was higher than that of CONV.

• Current efficiency decreased with increasing current density.  
→ H<sub>2</sub> evolution

## Conclusions

- No void was observed in the Sn film by EP-SCE because Sc-CO<sub>2</sub> dissolves H<sub>2</sub>.
- Grain size of EP-SCE and CONV are about 30 nm.
- Current efficiency of Sn EP-SCE was higher than CONV.

## References

- [1] T.F.M. Chang, M. Sone, A. Shibata, C. Ishiyama, Y. Higo, Electrochimica Acta, Elsevier 55 (2010) 6469-6475
- [2] T.F.M. Chang, M. Sone, Surface & Coatings Technology 205 (2011) 3890-3899