

# Towards Elimination of the Anode Effect and Perfluorocarbon Emissions from Hall-Héroult Cells

Hongmin Zhu & Donald R. Sadoway

Department of Materials Science & Engineering  
Massachusetts Institute of Technology  
Cambridge, Massachusetts  
U.S.A.

# background

- p on anode effect Hall-Héroult cell produces  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$  (PFCs)
- p PFCs have high GWP
- p in US, Al smelting is #1 point source of PFCs

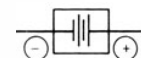
# premise of the current work:

- understanding the anode effect
- + understanding PFC generation
- + plan for reducing emissions



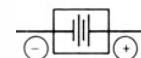
# outline of today's talk:

- p electroanalytical studies
- p gas analysis during electrolysis  
in laboratory cells
- p method to avert AE and PFC  
generation in lab cells
- p extension to industrial cells



# results of studies in lab cells

- p anodic reaction inhibited when potential exceeds a critical value,  $E_C \approx 3.0 - 3.5 \text{ V}$
- p anode becomes active again when potential is reduced below a so-called recovery value,  $E_R \approx 2.8 \text{ V}$
- p PFCs generated only at extreme potentials, i.e.,  $E > 4.0 \text{ V}$



# results of studies in lab cells

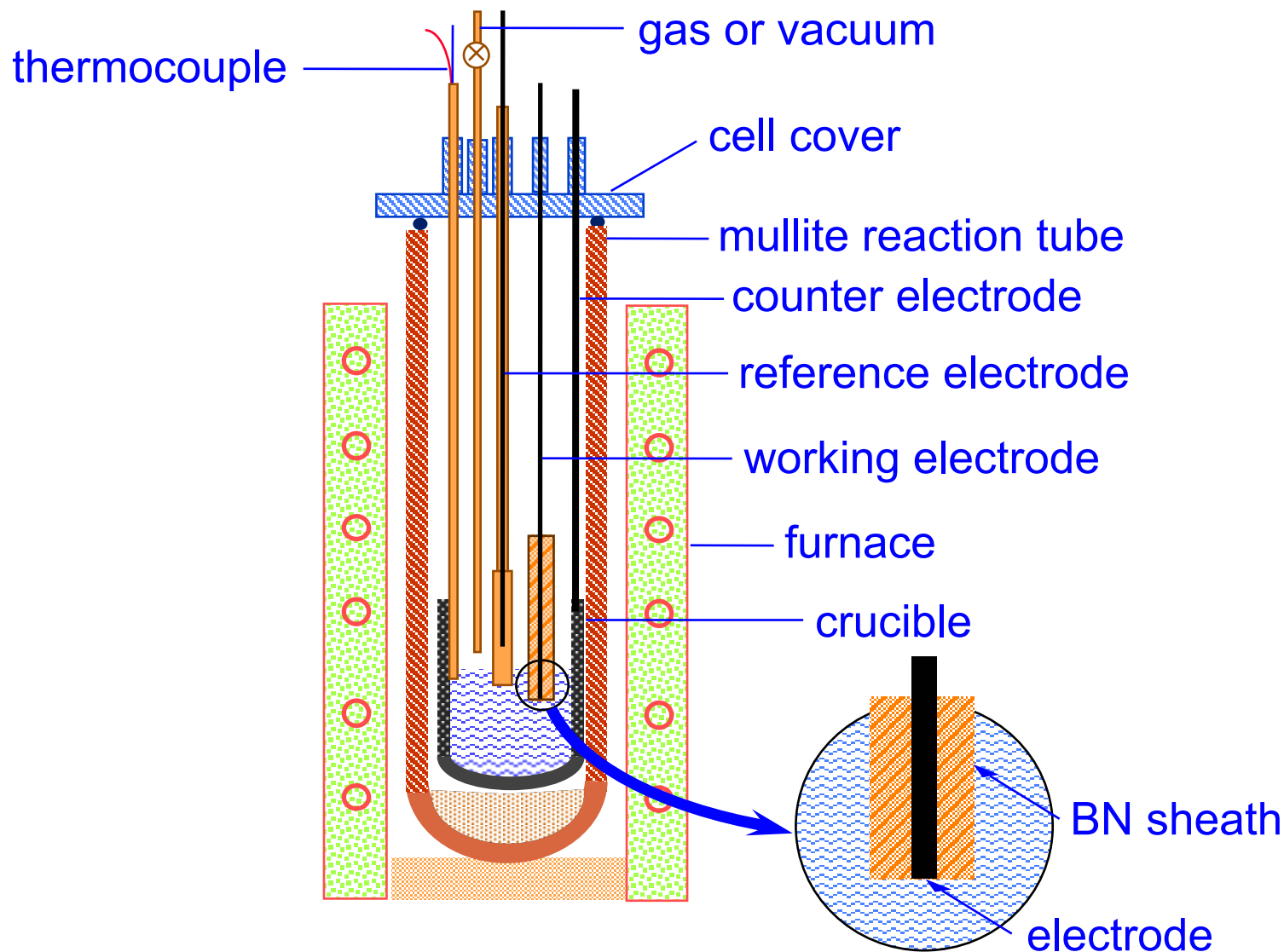
- + AE linked to formation of highly resistive surface film



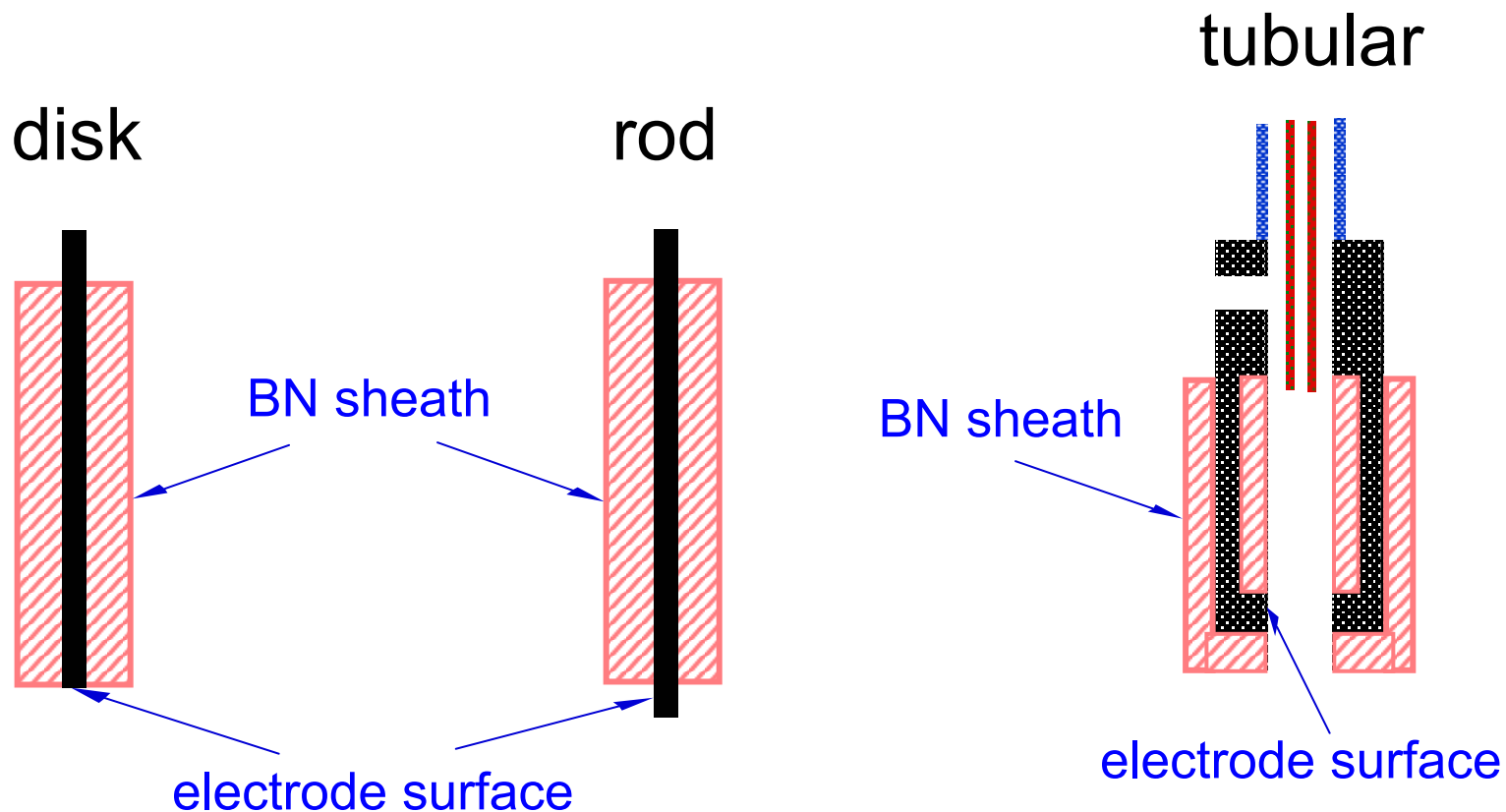
# our experiments:

- ☑ 3-electrode cell featuring
  - rotating rod anode (WE)
  - reference electrode
  - large counter electrode
  
- ☑ electrolysis cell featuring
  - tubular anode for improved gas sampling

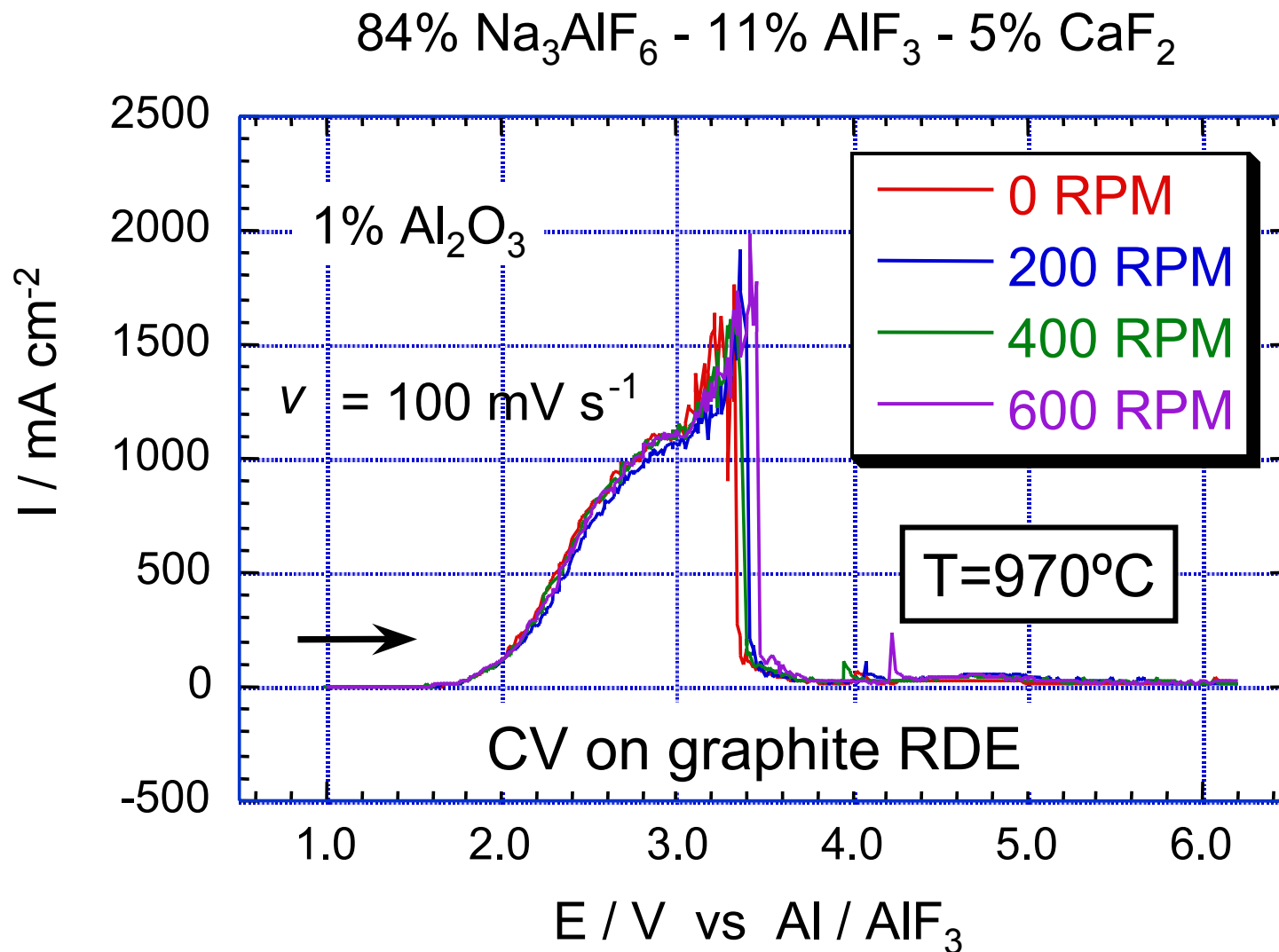
# cell for electrokinetic studies



# various types of electrodes

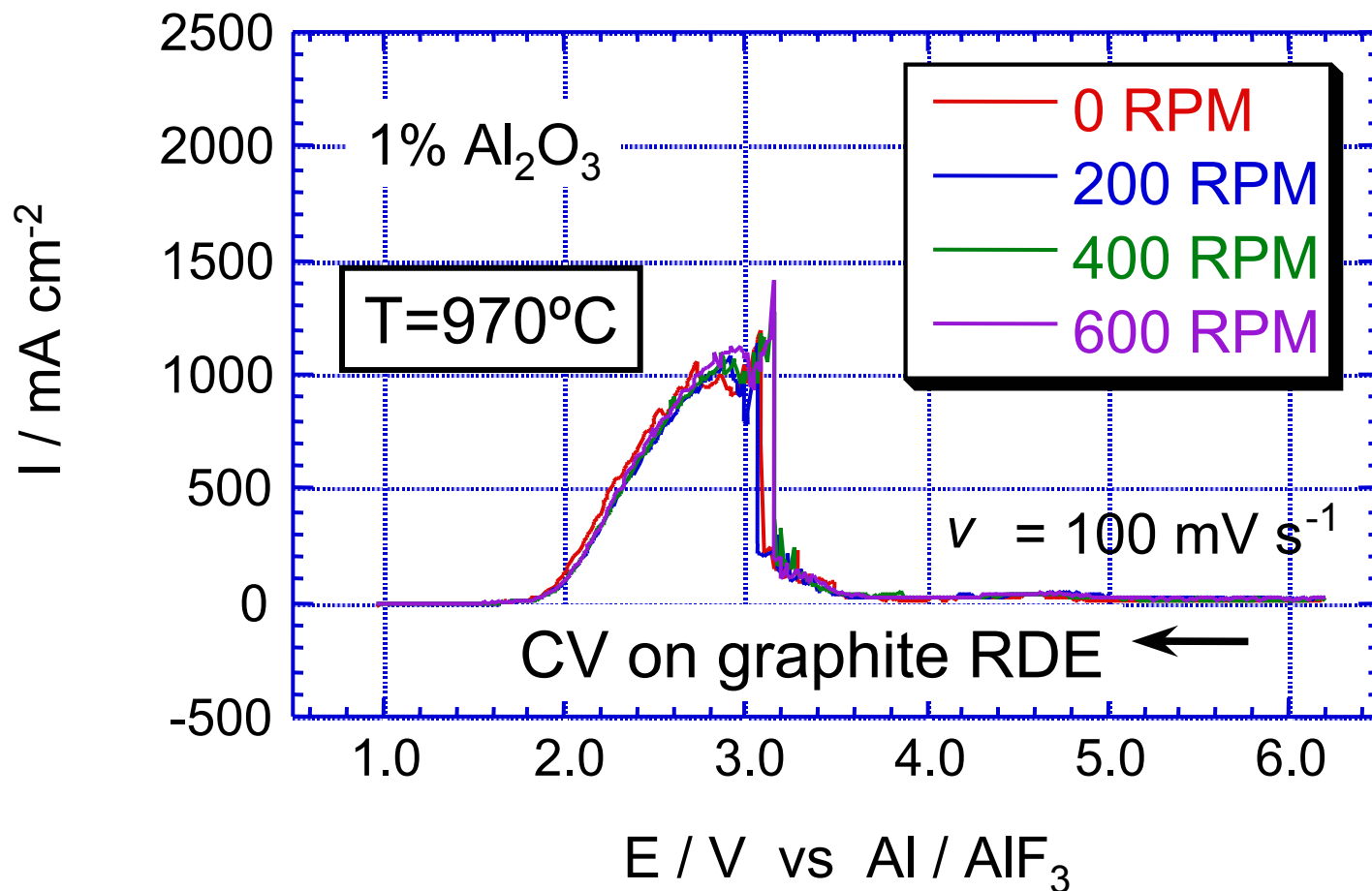


# evidence of a passivating film

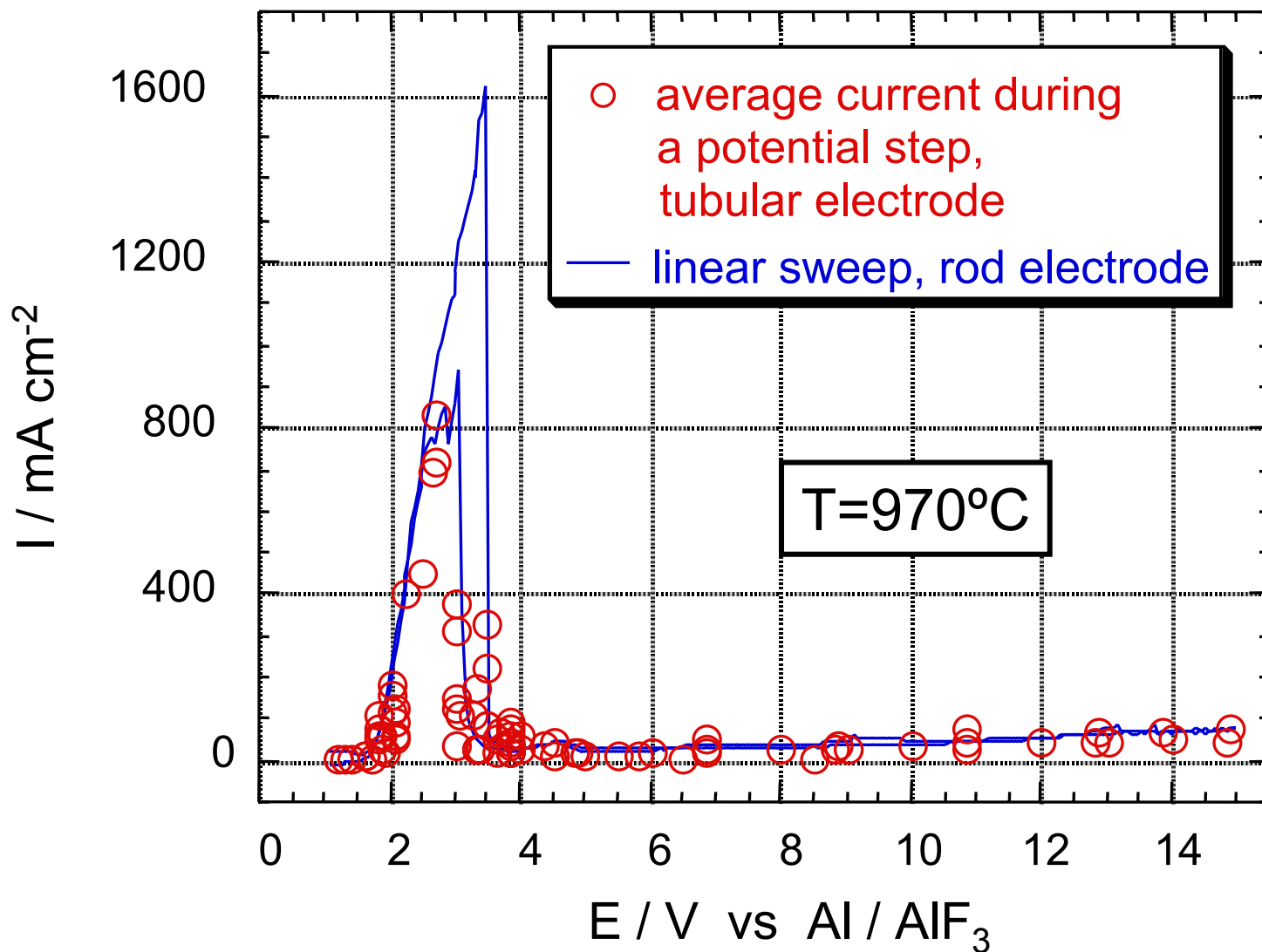


# evidence of a passivating film

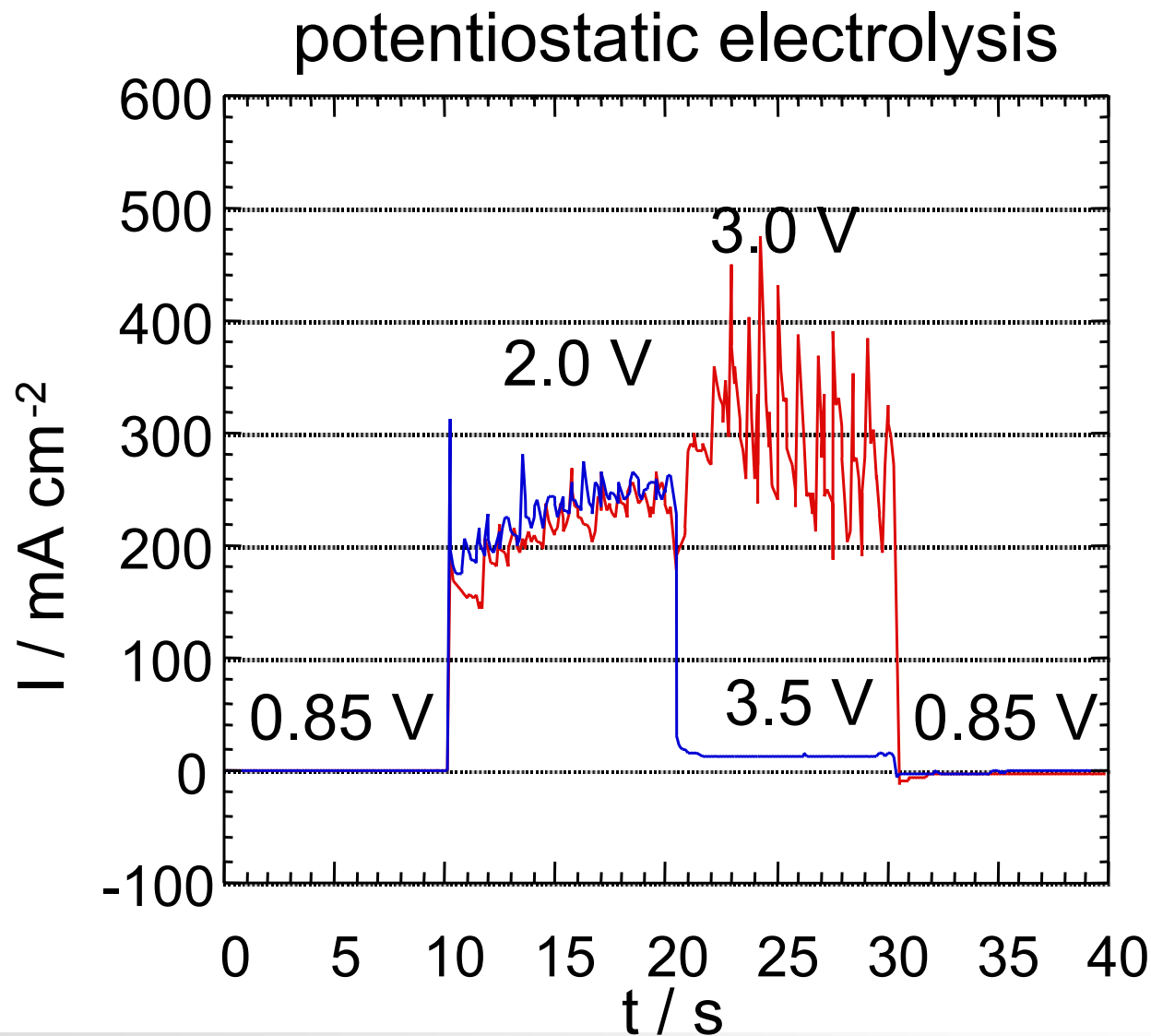
84%  $\text{Na}_3\text{AlF}_6$  - 11%  $\text{AlF}_3$  - 5%  $\text{CaF}_2$



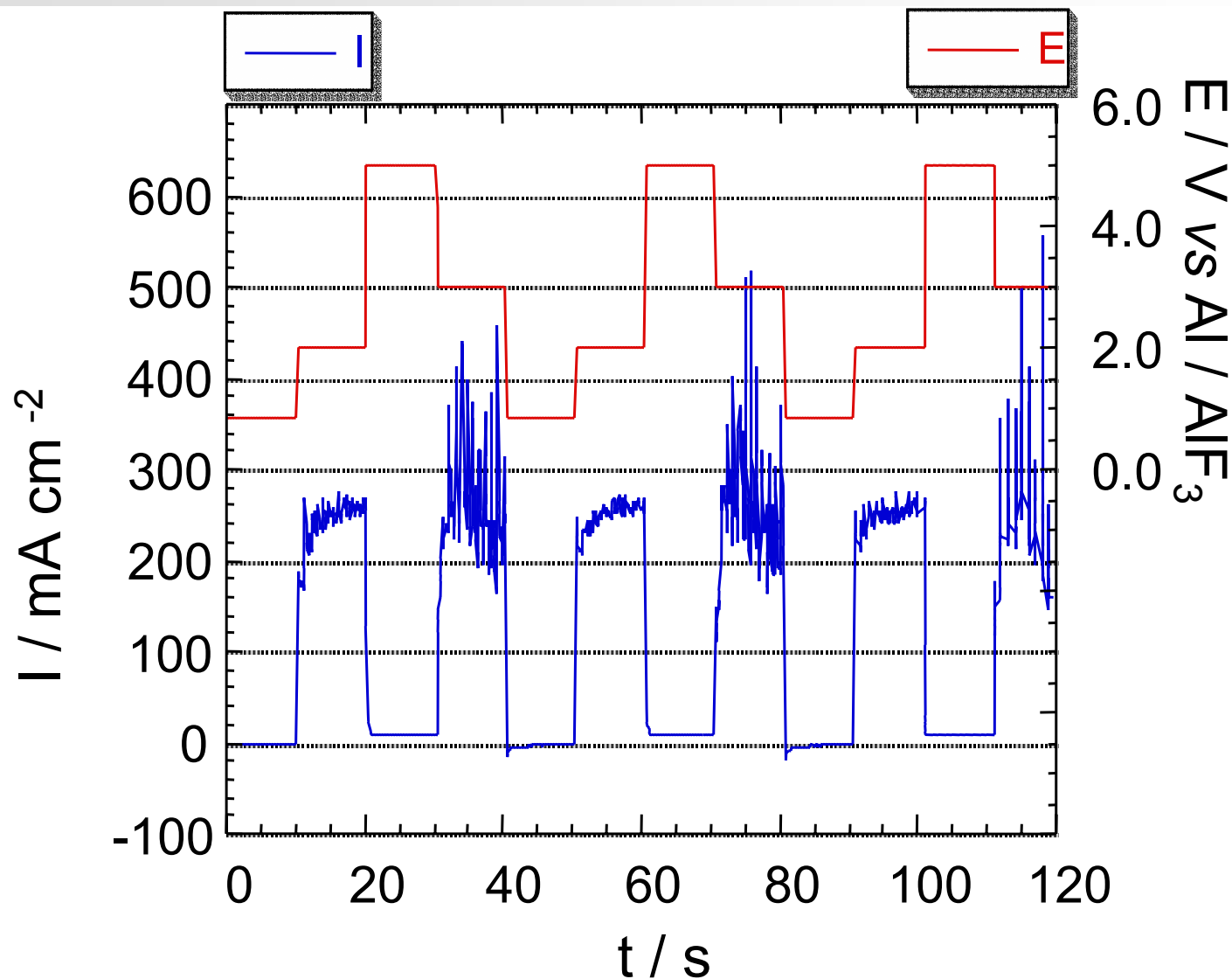
# evidence of a passivating film



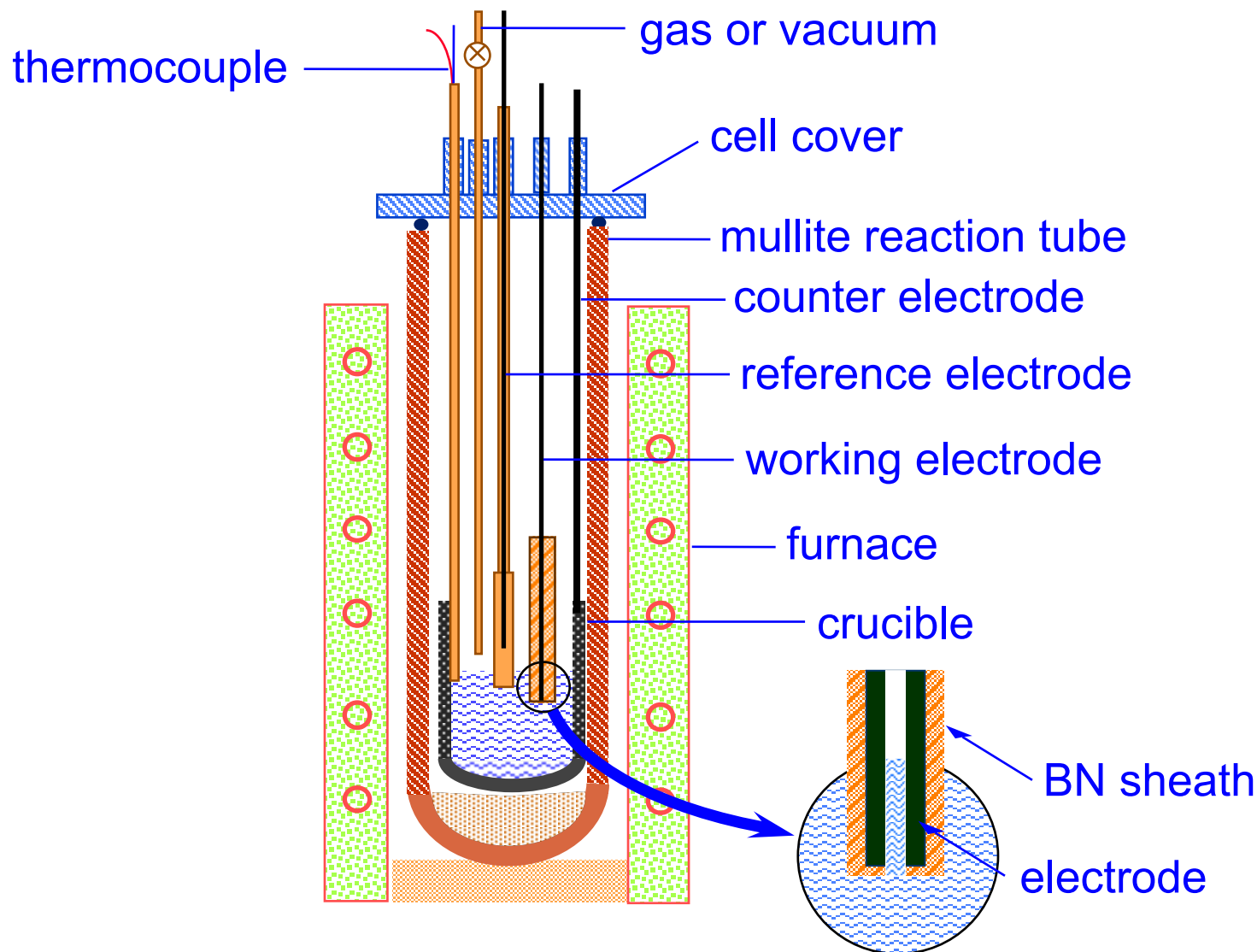
# evidence of film formation



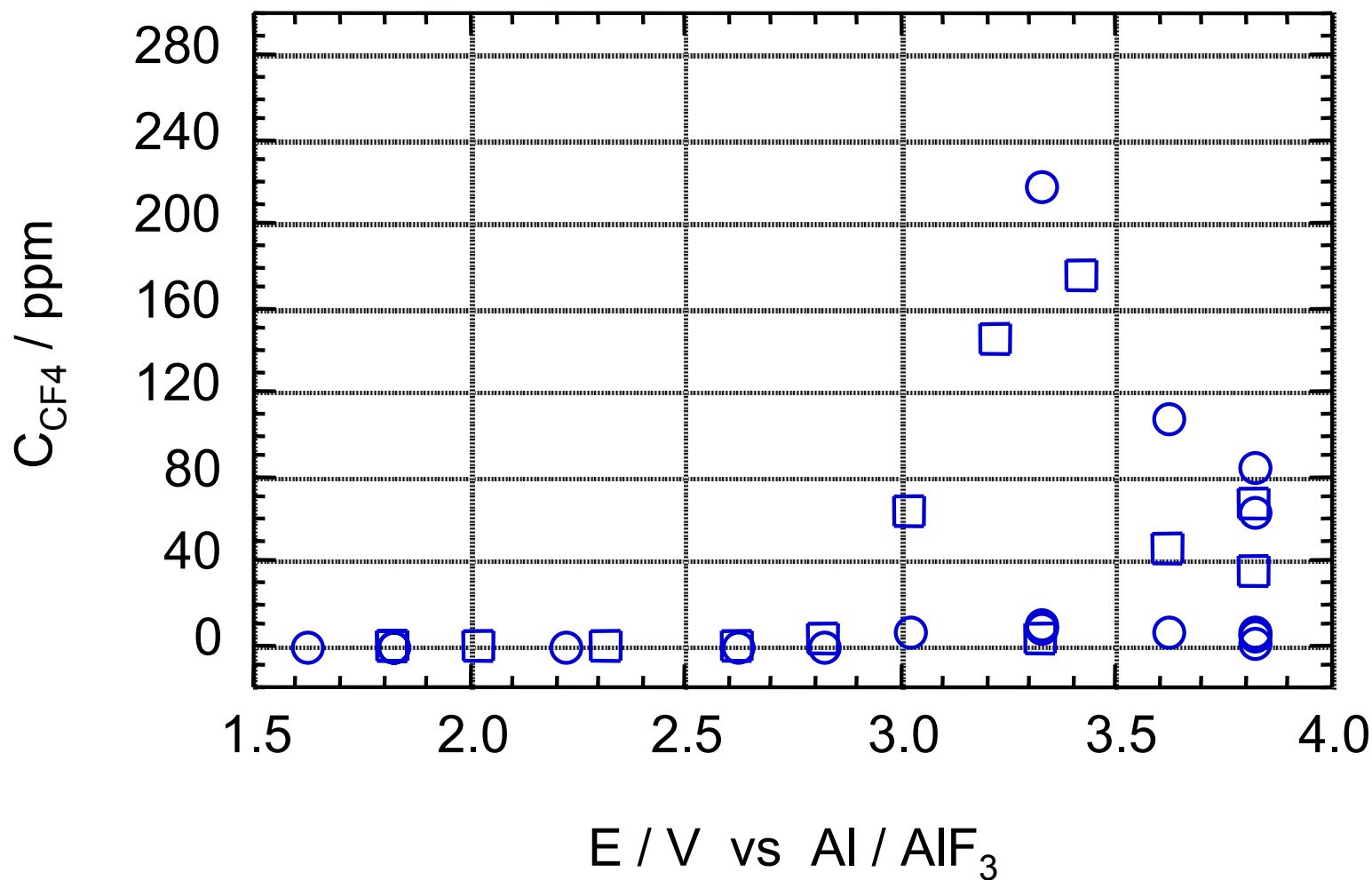
# evidence of film formation



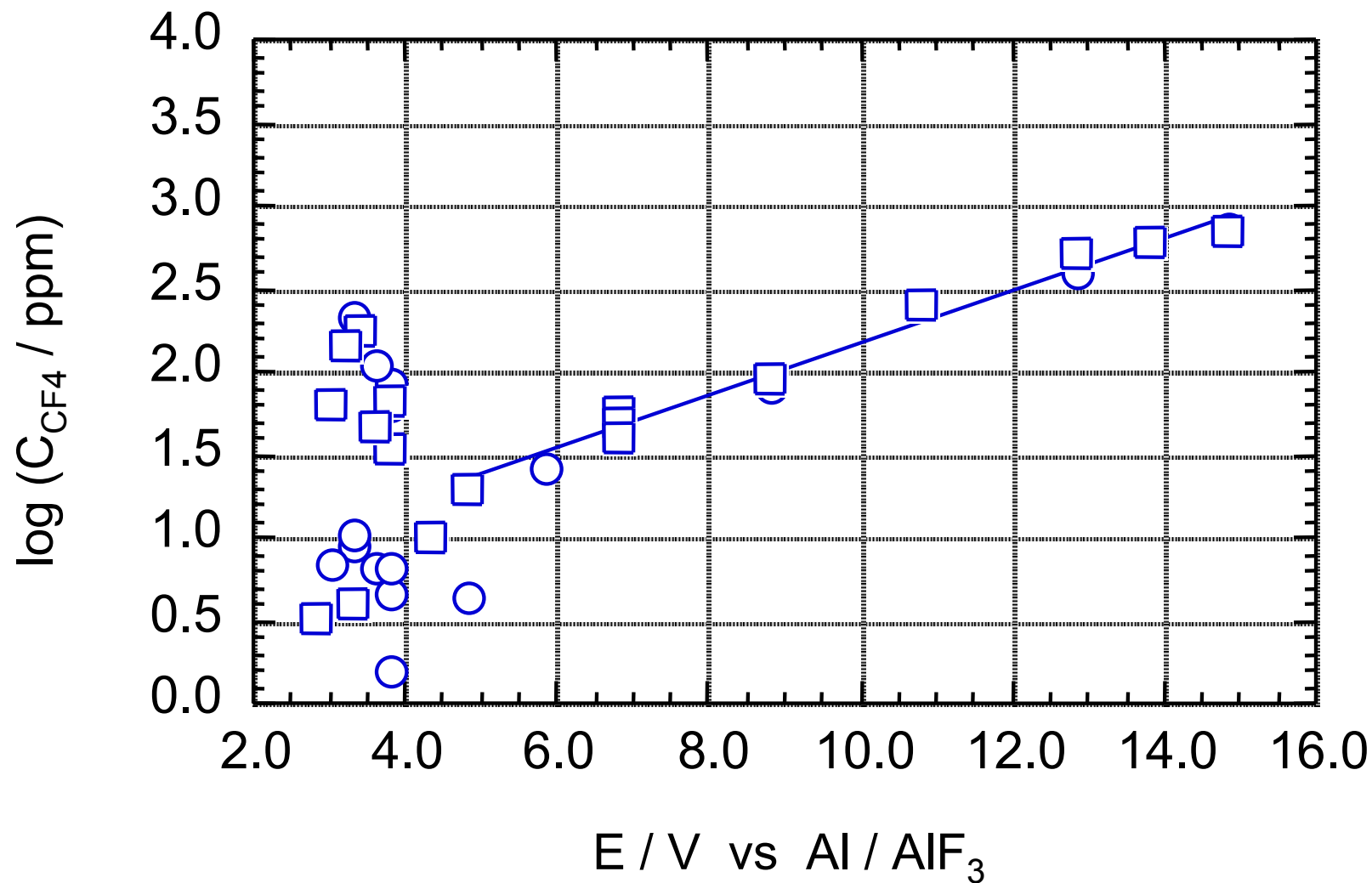
# cell for analysis of anode gas



# controlled-potential electrolysis



# controlled-potential electrolysis



# controlled-potential electrolysis

in the high-voltage regime

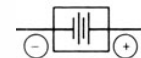
$$\ln c = \alpha + \beta E,$$

where  $\beta = 0.325 \text{ V}^{-1}$

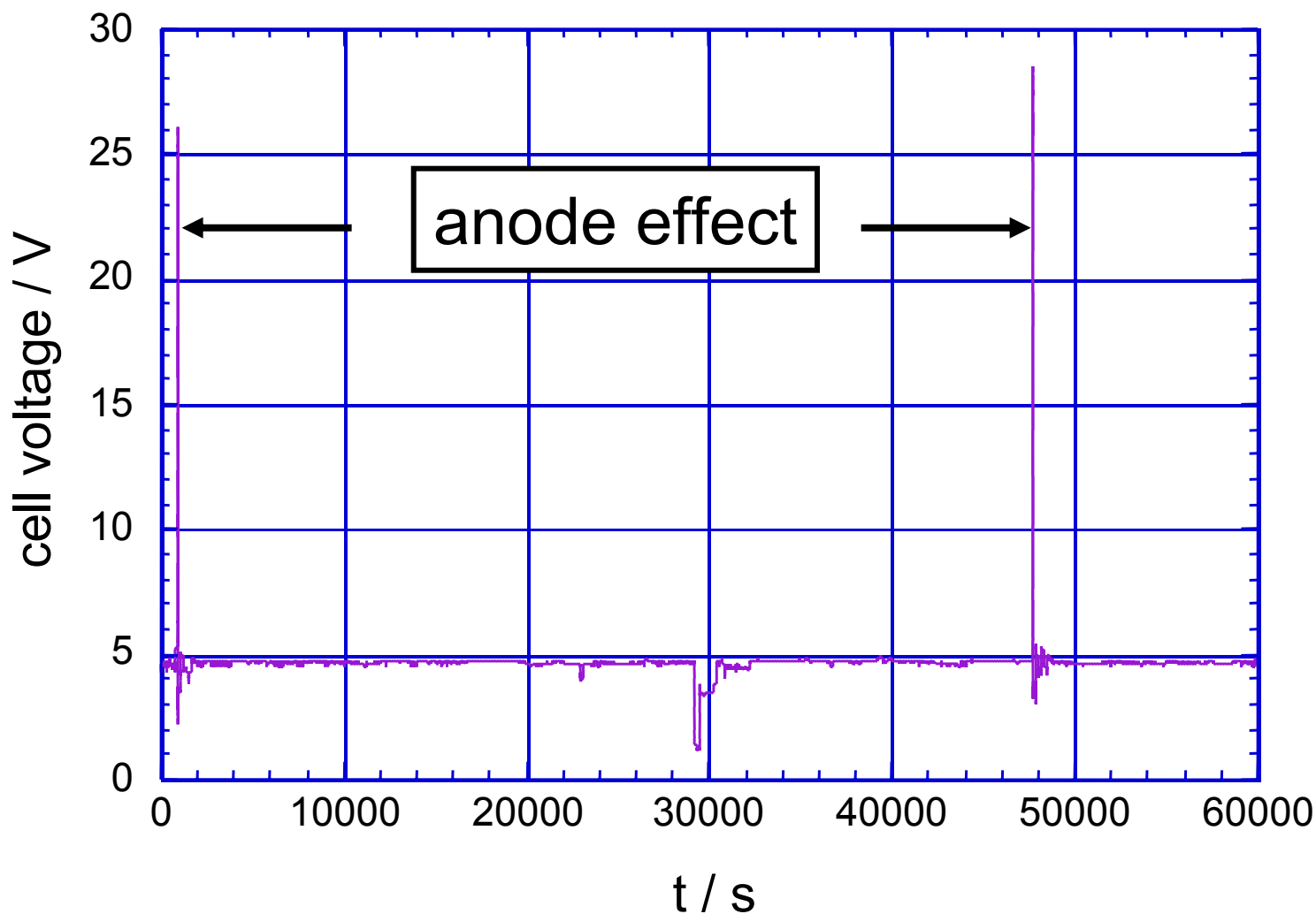
c.f. Nissen & Sadoway (1997)

$$r_{\text{CF}_4} = a \exp(b E),$$

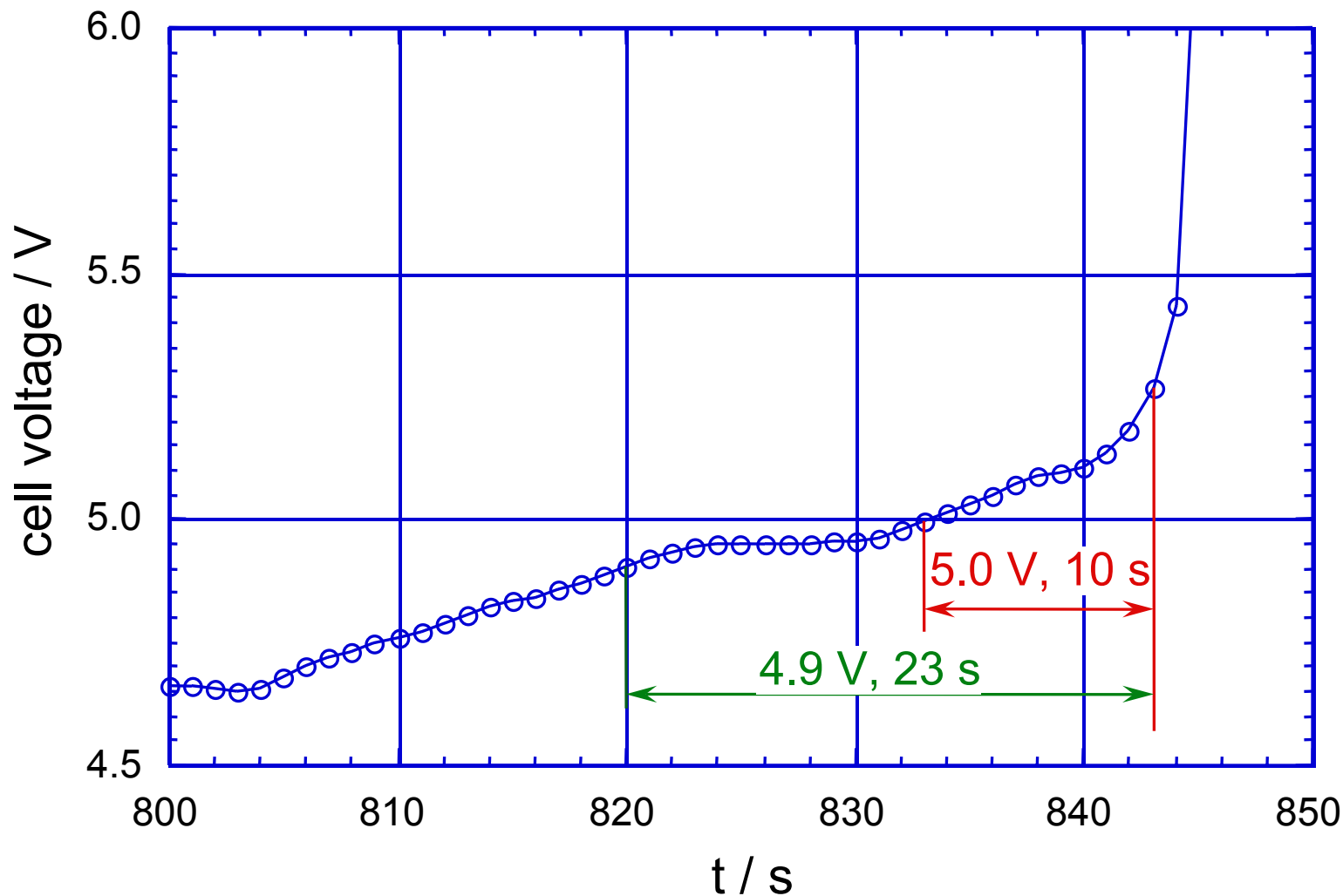
where  $b = 0.331 \text{ V}^{-1}$



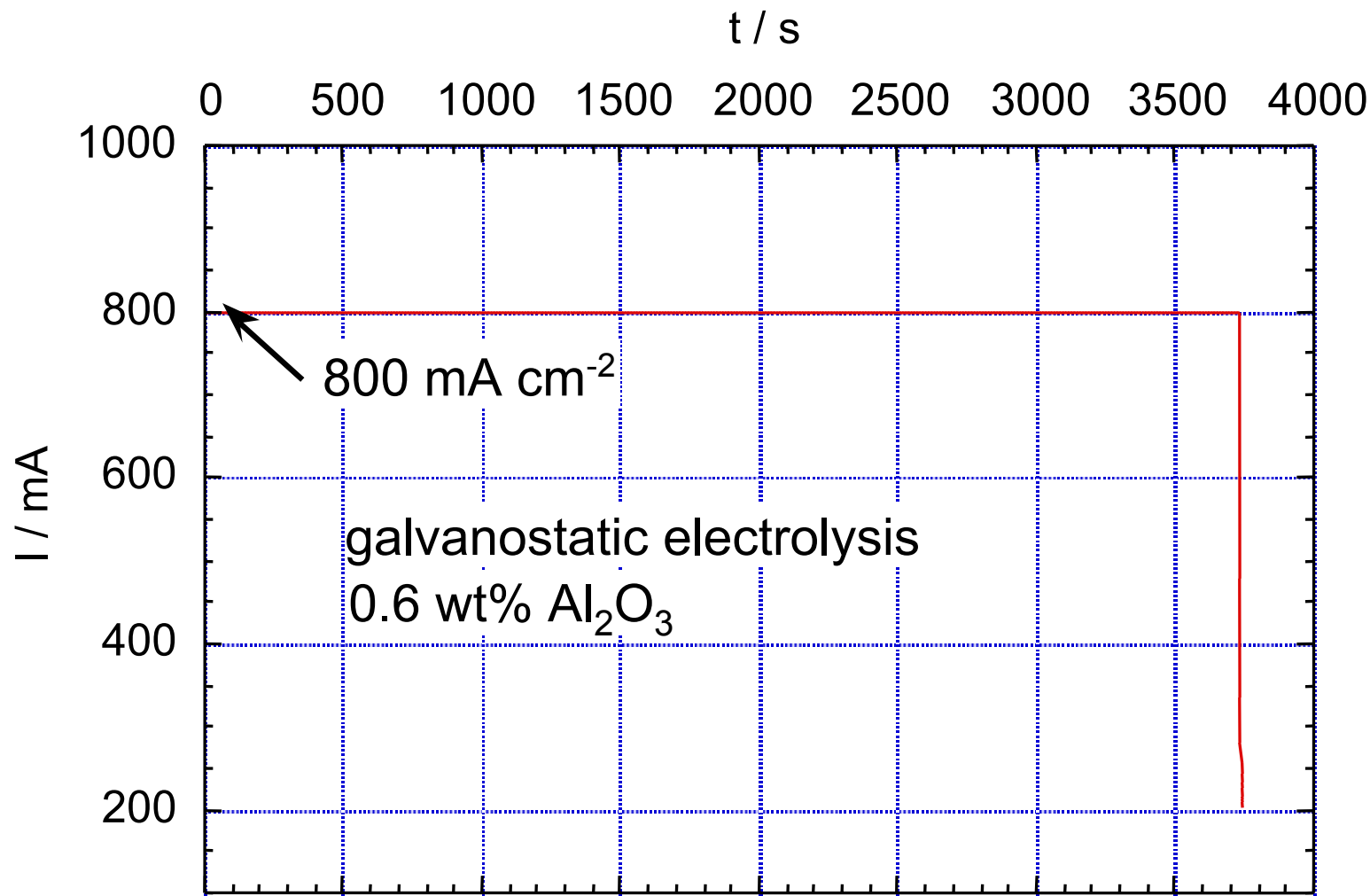
# data from an industrial cell



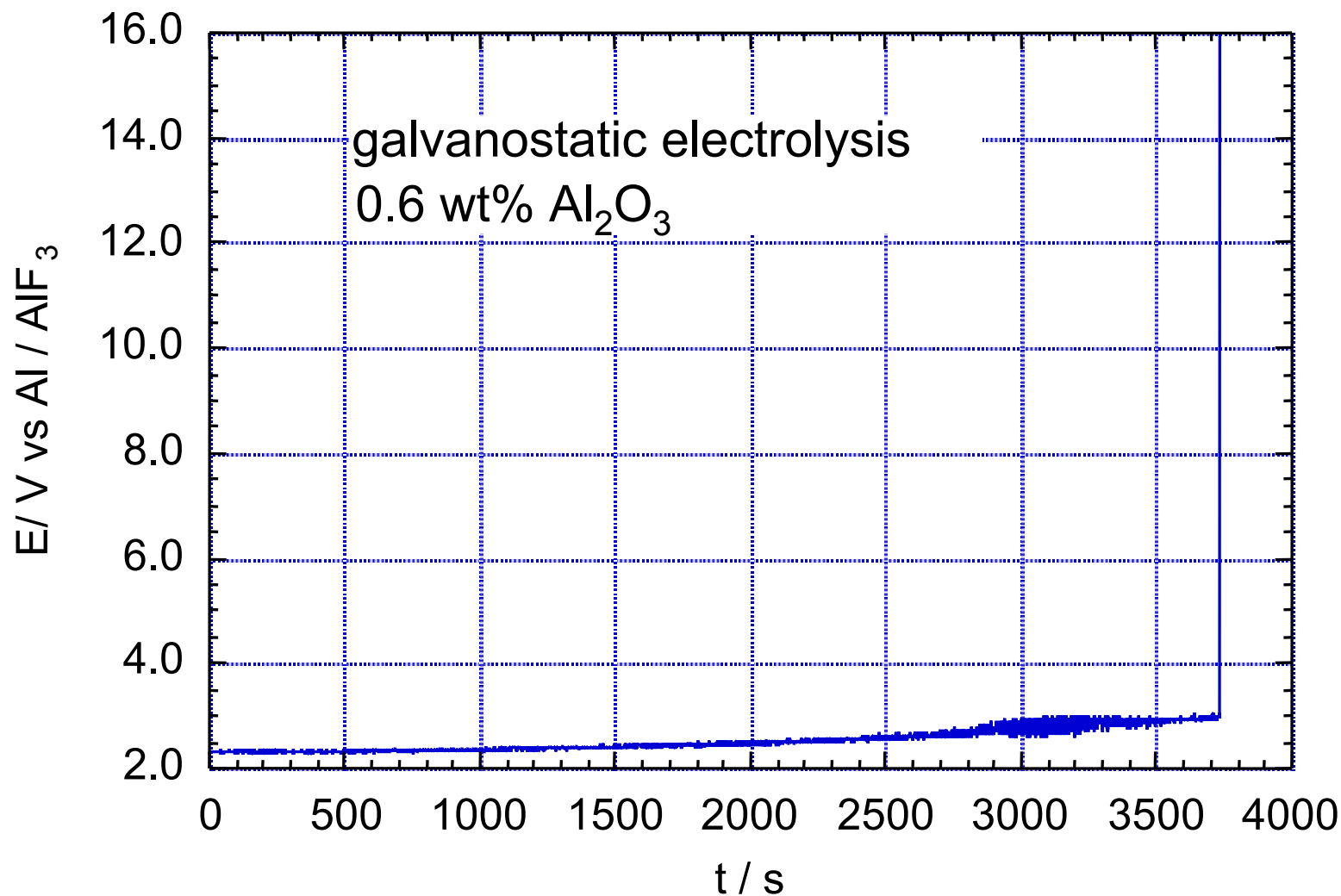
# a closer look at an anode effect



# data from a laboratory cell

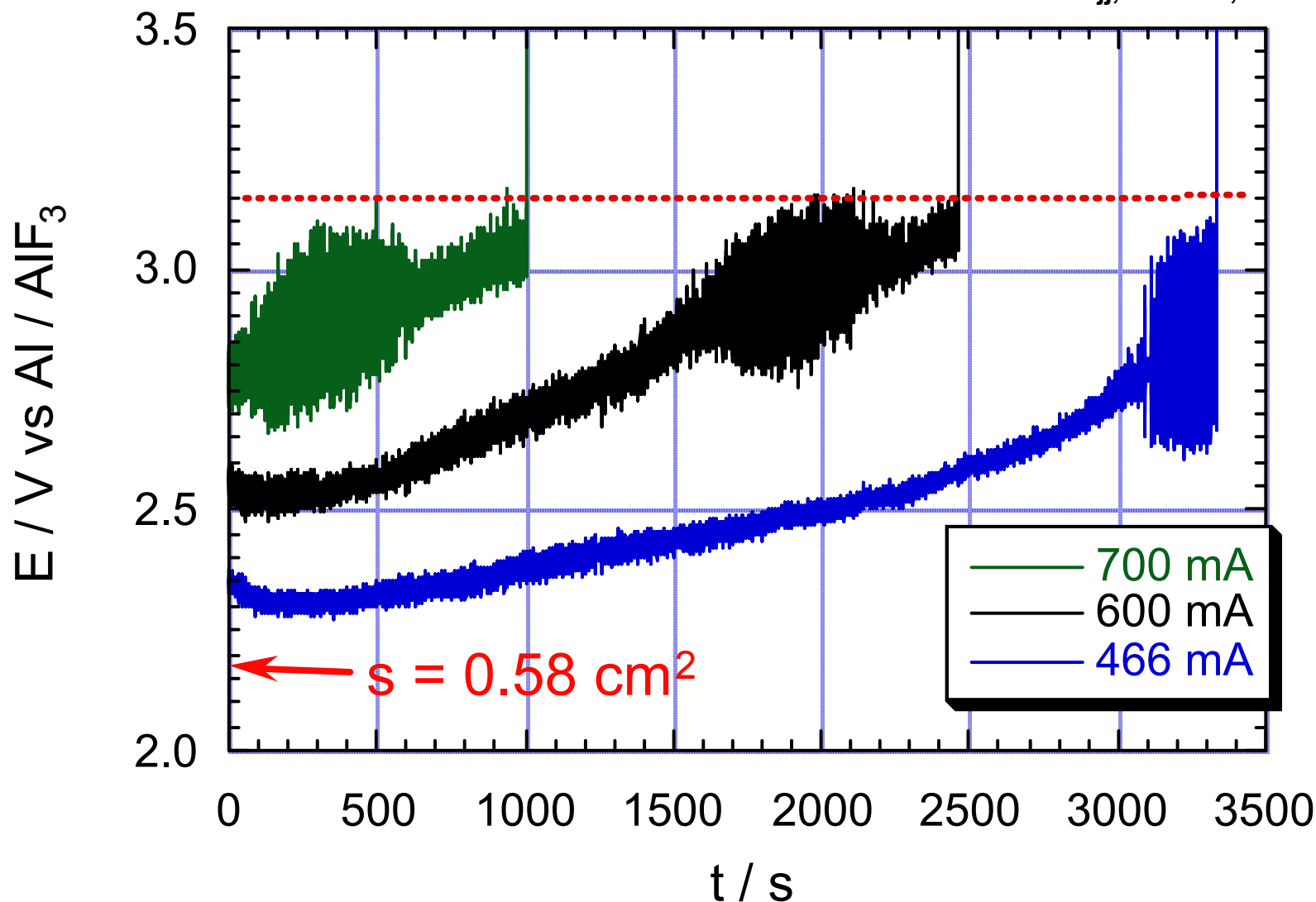


# data from a laboratory cell

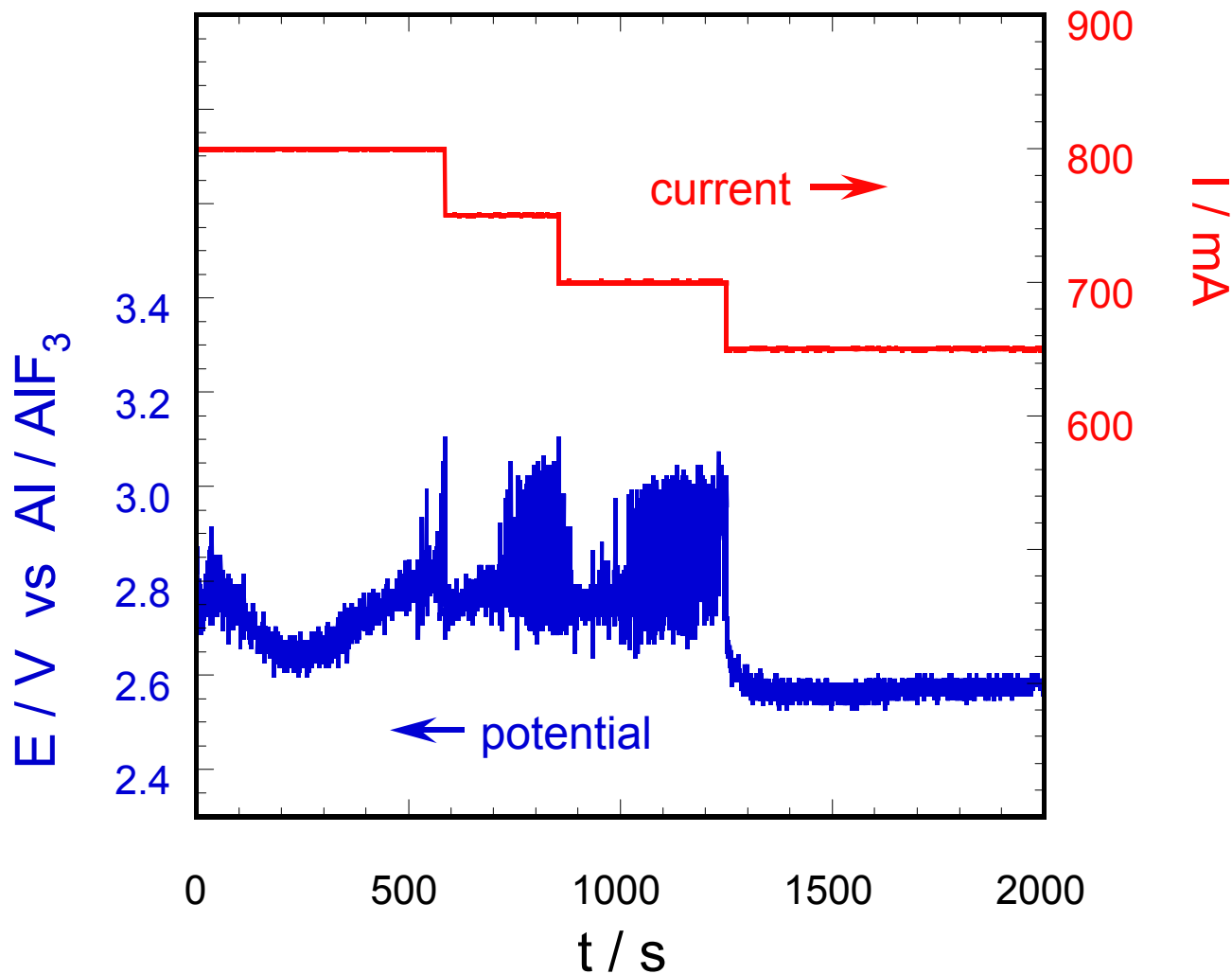


# data from a laboratory cell

9oc26jj, 9nv04ca, ha



# AE averted by current stepping



# major findings:

- ☑ onset of anode effect is potential dependent
- ☑ AE can be averted by reducing current so as to prevent voltage from exceeding a critical value

# in an industrial cell

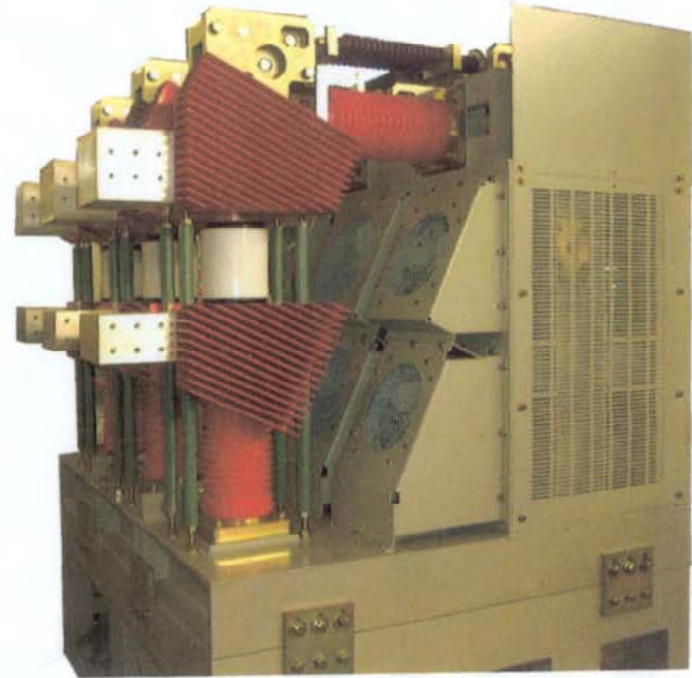
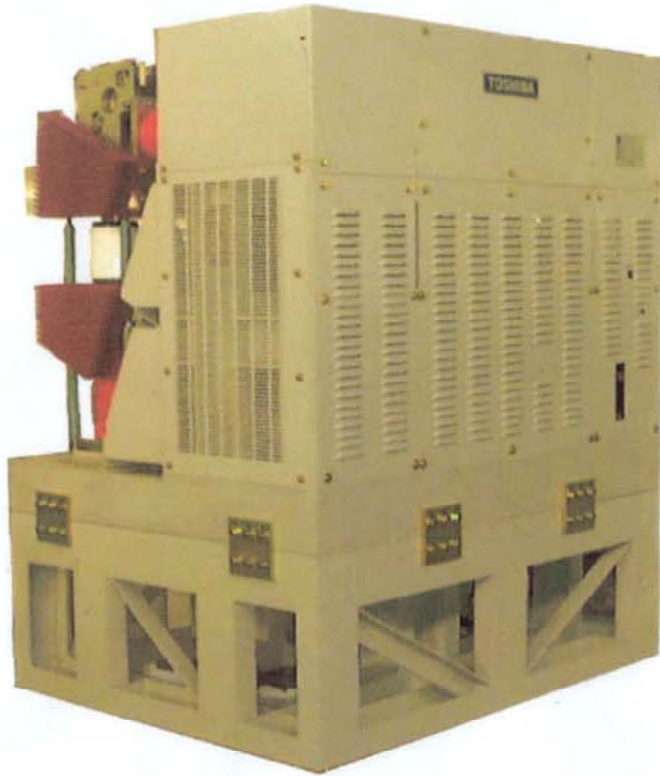
## enabling technologies:

- ☒ accurate voltage sensing
- ☒ control circuit
- ☒ robust current shunting



# vacuum current breaker

12kV-12000A 大電流通電器



# our proposal

☑ shunting  $\approx 1\%$  cell current  
drops cell voltage for  $\approx 1$  min

$\therefore$  300 kA cell  $\Rightarrow$  3 kA/min

$$\Rightarrow \frac{di}{dt} = 50 \text{ A s}^{-1}$$

+ **NO ANODE EFFECT!!!**

☑ no AE  $\Rightarrow$  no PFCs

# acknowledgments

The Aluminum Association

U.S. Environmental Protection Agency,  
Climate Protection Division

