First experience of HF concentration monitoring in KEK single-cell EP system

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Short summary

We analyzed HF concentration in the EP acid by Ion Capillary Electrophoresis (ICE).

We investigate relationship between cavity performance and the concentration.

We made important findings on EP acid life.

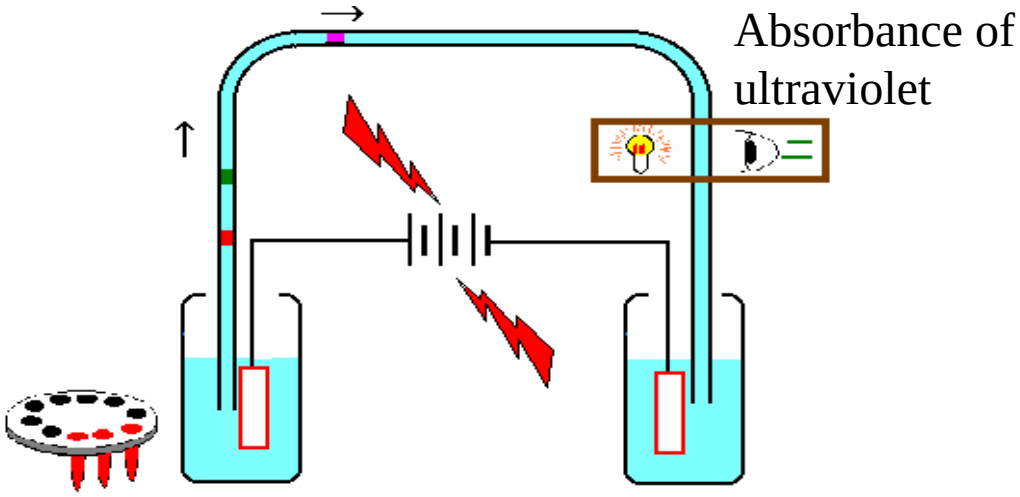
contents

1. Measurement method of F^- concentration in EP acid by Ion Capillary Electrophoresis (ICE) system.
2. Results of F^- concentration measurement in single-cell EP system at Nomura plating Co. Ltd.
3. Comparison of the measured F^- concentration in EP acid and the cavity performance.
4. Discussions for the extension of EP acid life time.
5. Summary

Ion Capillary Electrophoresis (ICE) measurement system.

CAPI-3300 System

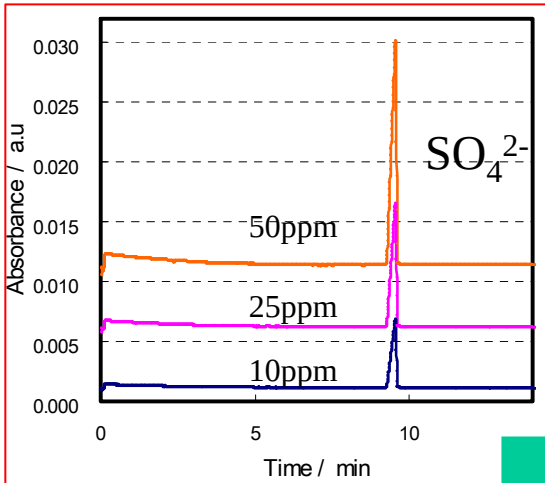
Outline figure of ICE system

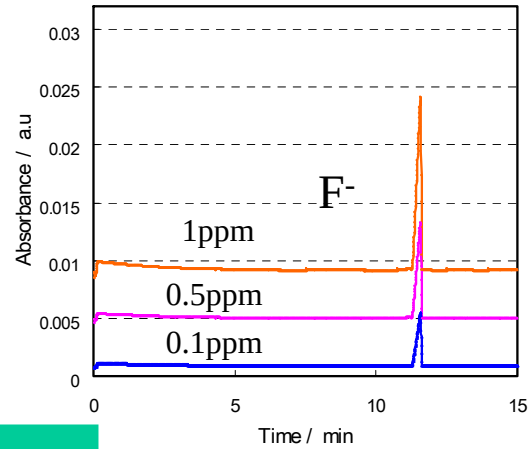


F^- and SO_4^{2-} in EP acid were measured by Ion Capillary Electrophoresis (ICE) measurement system.

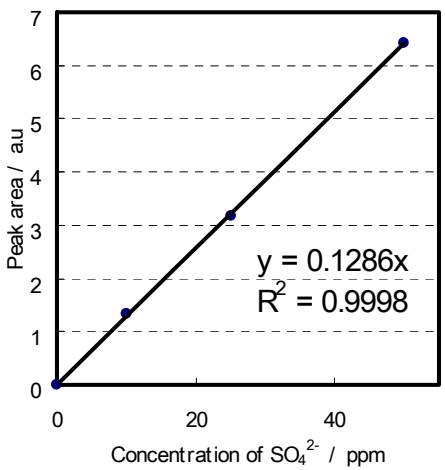
The schematic of Ion Capillary Electrophoresis (ICE) method is shown in the above right figure. Voltage is applied between both ends of capillary tube. Dissociation of ingredients occurs according to the difference of adsorption and desorption in a capillary tube. Ingredients move in the tube and different ingredients are separated/identified by different arriving time at the measuring point of absorbance of ultraviolet.

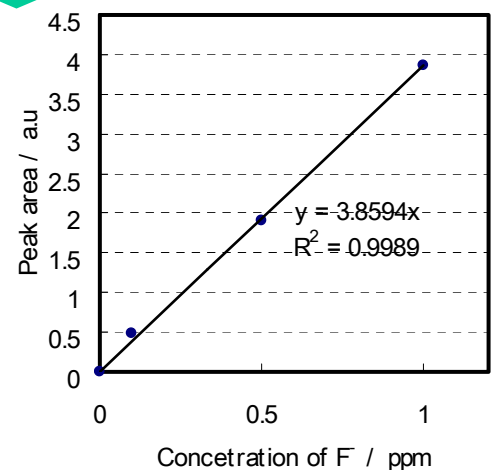
Separation and quantitative measurements of F^- and SO_4^{2-}



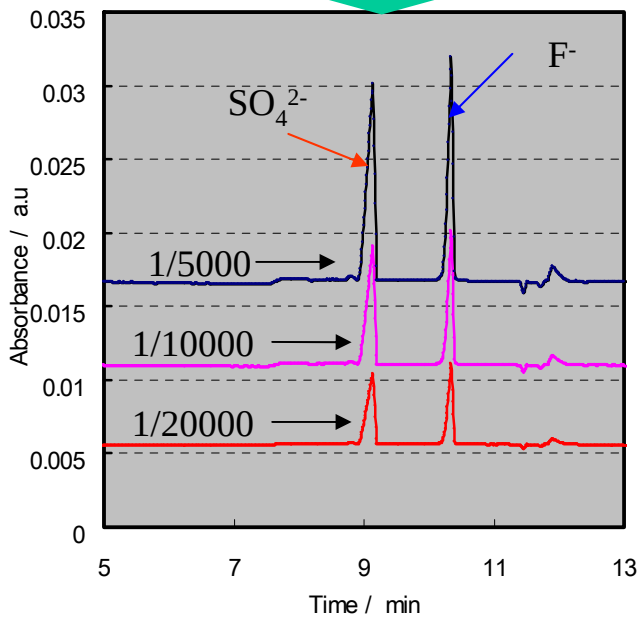


We made the calibration functions of SO_4^{2-}, F^- for quantitative measurements by ICE.





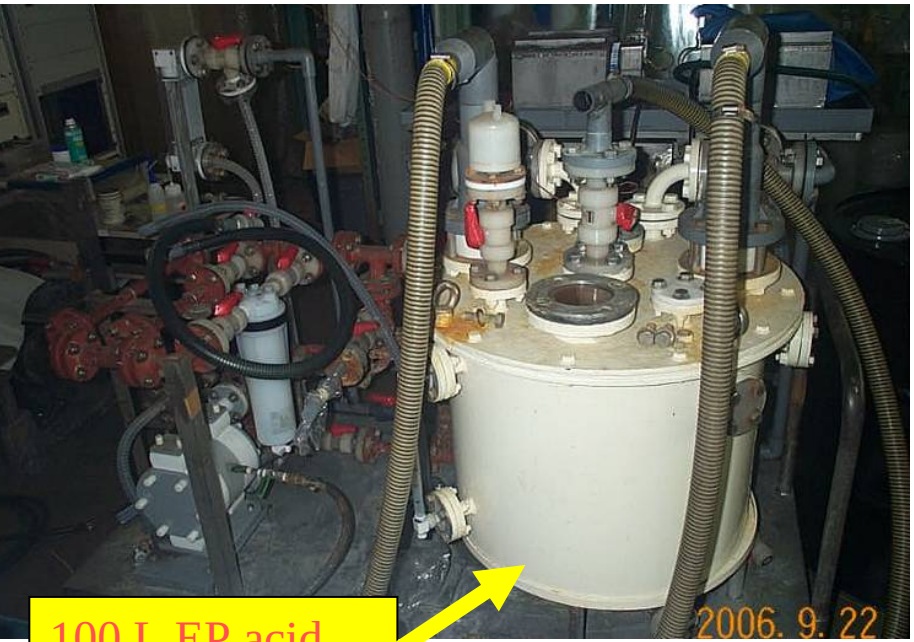
We could separate SO_4^{2-} and F^- in EP acid by ICE, and we also made the calibration functions of SO_4^{2-} and F^- for the quantitative measurements .



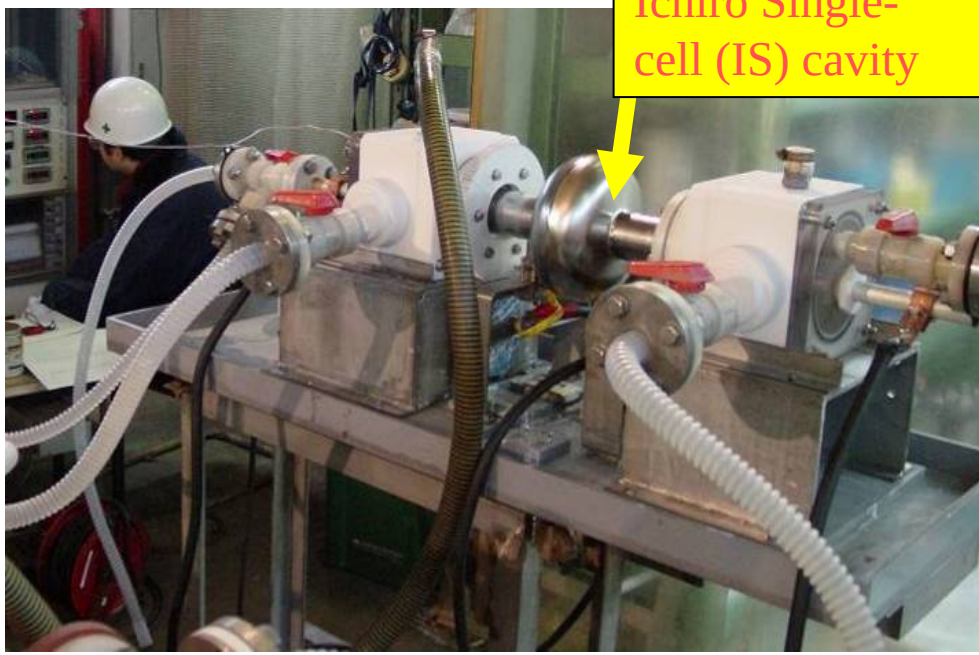
In this study, we performed the measurements of F- concentration in the EP acid with this calibration function.

Analysis of EP acid in Nomura plating Co. Ltd.

We measured F^- concentrations in EP acid by ICE after each electropolishing (EP) of Nb single-cell cavities. The EP system is shown in the figure below.



100 L EP acid reservoir tank



Ichiro Single-cell (IS) cavity

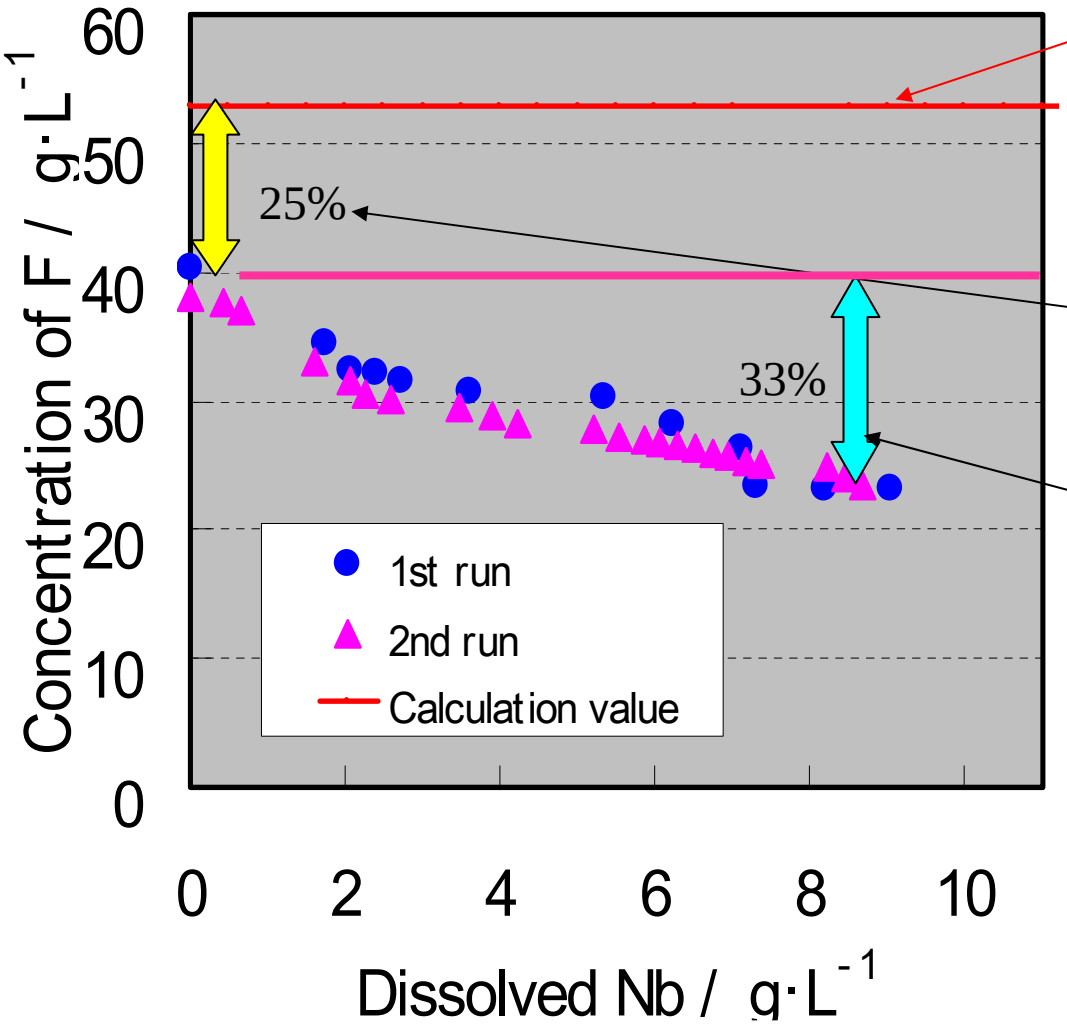
This experiment is combined to KEK Single-cell S0 study .

KEK S0 Single Cell Study

	Eacc,max [MV/m] / Qo @ Eacc,max									Emax average [MV/m]	Scatt. [%]	MP	Acceptability @ 40M V/m [%]
	IS#2	IS#3	IS#4	IS#5	IS#6	IS#7	IS#8	CLG#1	CLG#2				
CBP+CP+AN+EP(80) +HPR+ Bake	36.9	31.4	45.1	44.2	48.8	28.3				39.1 ± 8.2	21	Yes	50
	1.53e10	8.66e9	9.07e9	5.38e9	9.64e9	1.94e9							
CBP+CP+AN+ EP(80+3 fresh) +HPR+Bake		42.0	46.1	44.3	34.3	39.3			43.8	41.7 ± 4.4	11	Yes	67
		9.72e9	9.47e9	1.08e10	8.56e9	1.03e10			3.46e9				
CBP+CP+AN+ EP(40+3 fresh) +HPR+Bake	43.9						49.2*			46.6 ± 3.7	8	Yes	100
	9.47e9						4.33e9						
+EP(20+3 fresh)+HPR +HF+Bake	47.1	44.7	47.8		48.6	43.9		47.9		46.7 ± 1.9	4	Yes	100
	1.06e10	9.80e9	7.80e9		8.00e9	1.17e10		1.00e10					
+EP(20)+HPR+Bake	47.2	52.2	52.9	31.1	48.9	46.5				46.4 ± 8.0	17	Yes	83
	5.98e9	1.51e10	5.23e9	5.21e9	7.56e9	9.03e9							
+EP(20)+Degreasing (US)+HPR+ Bake		50.1	52.2							51.2 ±1.5	2.9	Yes	100
		7.80e10	7.08E9										
+EP(20)+H2O2+HPR + Bake	52.3			34.1	43.4	40.9				42.7 ± 6.0	18	No/Yes	50
	1.09e10			1.37e10	1.39e10	3.01e9							
EP(20)+Degreasing+ H2O2+HPR+Bake													
Others													

This EP acid analysis is combined to KEK Single-cell S0 study .

Results of total F^- concentration measurement at Nomura



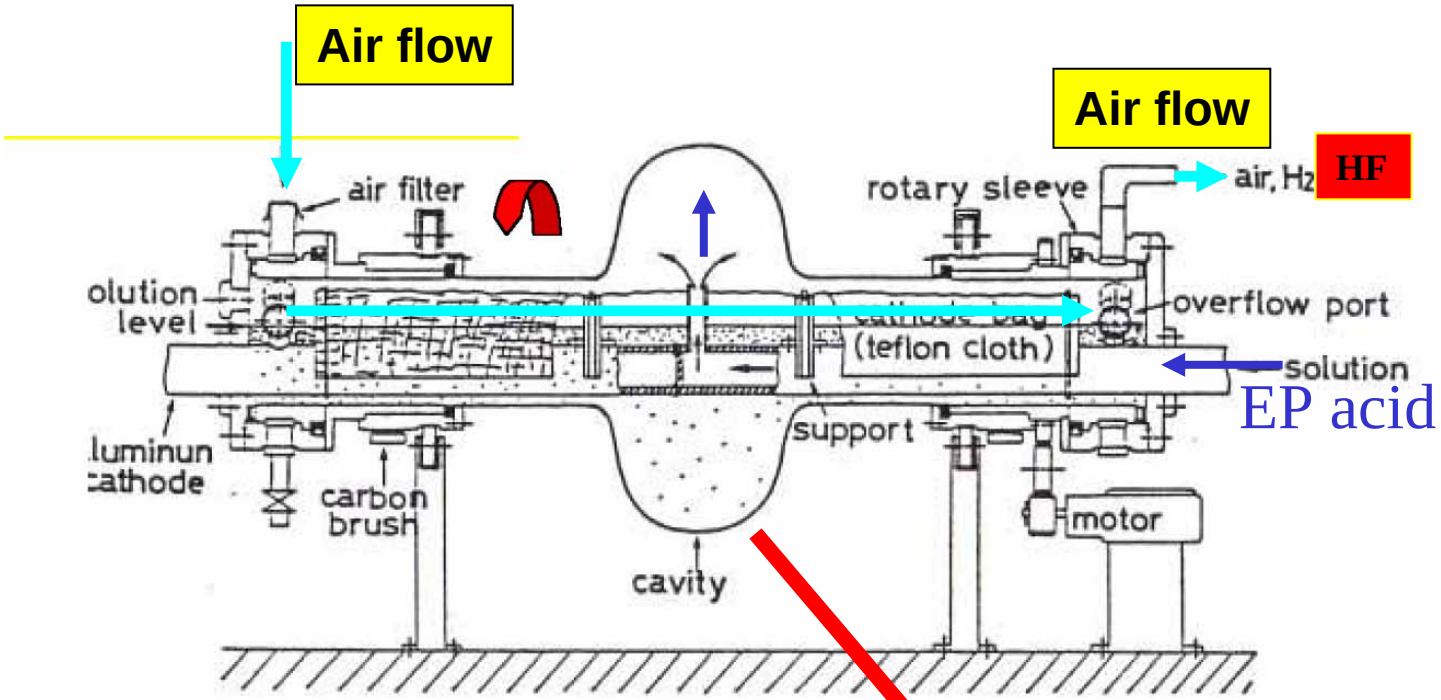
Calculated total F- concentration for HF : H_2SO_4 = 1 : 10.(No HF evaporation case)
Total F is constant during EP process.
(TTC at KEK 25.Sep.2006)

Evaporation during making EP acid.

Evaporation during EP process .
Air flow in EP system?

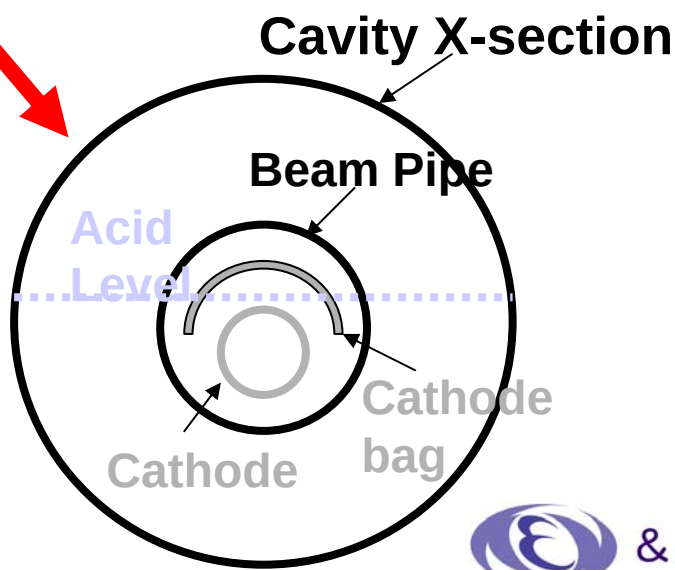
Finding1: 25% of HF escaped when EP acid was prepared. 33% of HF escaped during EP process .

Horizontally Rotated Electro-Polishing (EP) at Nomura



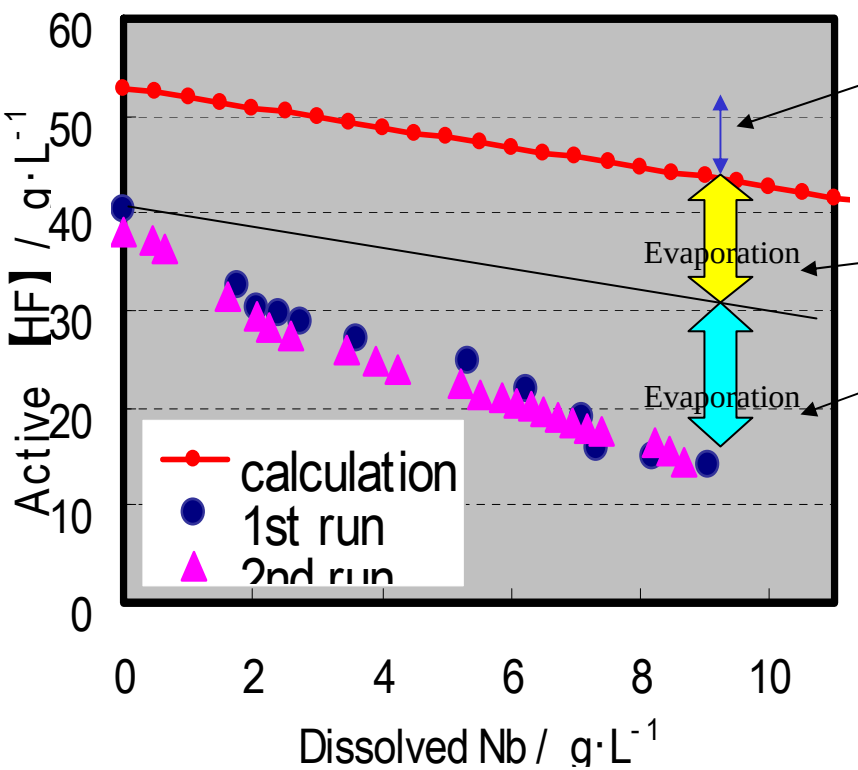
During EP process, there is air flow inside cavity above EP acid surface.

Right figure is cavity X-section. Lower half is filled with EP acid and upper half is the flowing air.



Relation of dissolved Nb and active 【HF 】 concentration

Active HF in EP acid is estimated.



Red line indicates the calculated active 【HF】 in EP acid for the ratio of HF : H_2SO_4 = 1 : 10.

As EP process advanced, active 【HF】 is used and decreases.

Evaporation during making EP acid.

Evaporation during EP process .
Air flow in EP system?

We assumed that all dissolved Nb in EP acid form NbF_5.

We also assumed that active 【 HF 】 which can be used for EP process is the 【 F^- 】 which does not form NbF_5 .

Active 【HF (g/L)】 = 【F-(g/L)】 - 5 ×(19.0/92.9) × 【 Nb^{5+}(g/L)】

= 【F-(g/L)】 - 1.02 × 【 Nb^{5+}(g/L)】

Finding 2 A half of Active 【HF】 escaped when dissolved Nb reached to 9 g/L at the end of EP process.

Measured concentrations of EP acid and cavity performance

Treatment day of EP	Dissolved Nb (g/L)	Concentration of F- (g/L)	Concentration of Active [HF] (g/L)	Concentration of SO_4^{2-} (g/L)	Eacc [MV/m]
2006/6/21	0.00	40.32	40.32	1492.8	
2006/7/10	2.07	32.30	30.19	1498.5	48.50
2006/7/24	2.40	32.14	29.69	1506.5	35.80
2006/7/25	2.73	31.55	28.77	1305.3	41.39
2006/7/26	3.60	30.65	26.98	1457.6	46.10
2006/9/6	6.22	28.15	21.80	1486.2	39.30
2006/9/7	7.09	26.33	19.10	1541.3	42.00
2006/9/19	8.18	23.31	14.97	1435.6	44.73
2006/9/20	9.05	23.29	14.06	1586.4	34.25
2006/9/29	0.00	38.10	38.10	1608.1	
2006/11/3	2.05	31.60	29.51	1558.4	49.20
2006/11/8	3.47	29.40	25.86	1563.1	43.80
2006/11/10	3.91	28.90	24.91	1542.9	45.01
2006/12/21	6.07	26.81	20.62	1529.0	45.77
2006/12/22	6.29	26.51	20.09	1531.4	48.64
2006/12/25	6.51	26.31	19.67	1548.1	42.68
2007/1/29	6.73	25.85	18.99	1521.9	52.24
2007/1/30	6.95	25.65	18.56	1511.4	52.91
2007/1/31	7.17	25.23	17.92	1574.3	31.1
2007/2/1	7.38	25.05	17.52	1504.9	48.9
2007/2/9	8.45	24.12	15.50	1557.8	46.5
2007/2/20	8.68	23.35	14.50	1547.9	43.35

1st run

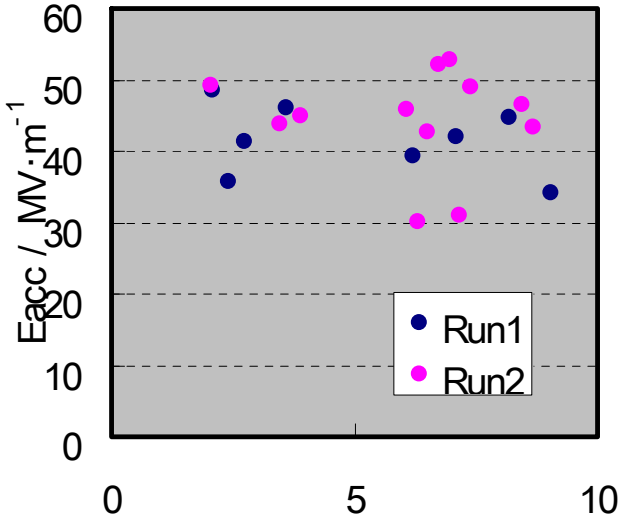
2nd run

Conditions

Material : polycrystalline

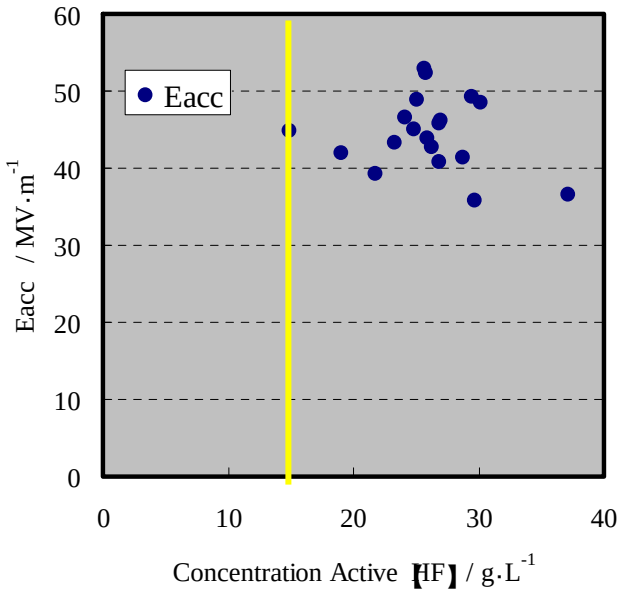
Cavity Shape : Ichiro Single-cell (IS) / Low Loss (LL)

Comparison of dissolved Nb,Active 【HF】 and cavity performance



There is no correlation between dissolved Nb and cavity performance up to the dissolved Nb of 9 g/L.

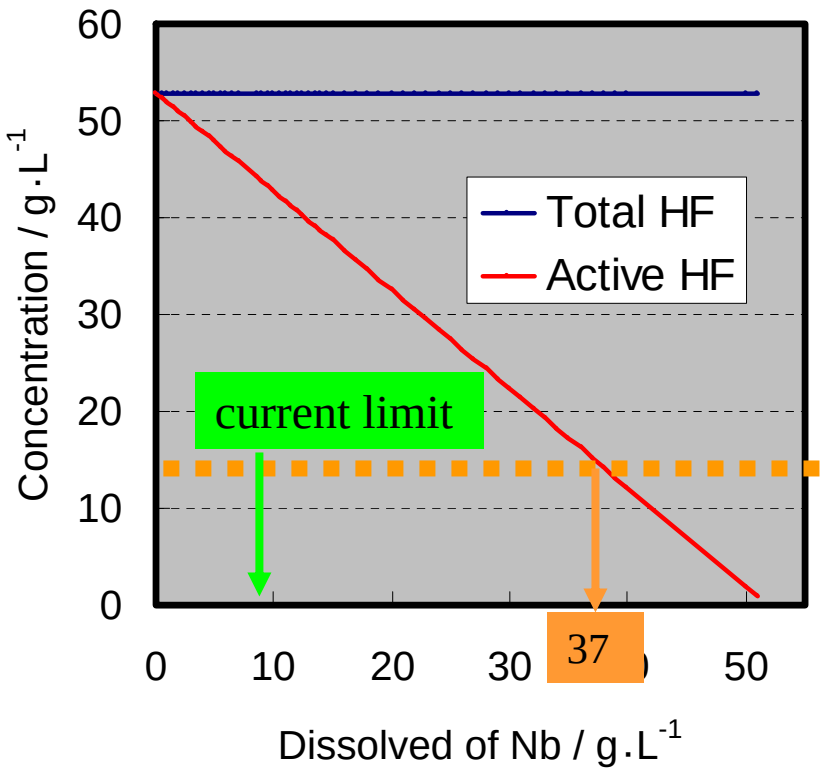
Finding3 : The dissolved Nb of 9 g/L is still OK.



In the EP process of Nomura plating Co. Ltd., this region of dissolved Nb corresponds to the Active HF concentration >15 g/L.

The region of dissolved Nb > 9 g/L and active HF < 15g/L should be explored in further experiment !

Discussions for the extension of EP acid life time



15 g/L

Cavity performance limit

37 g/L (ideal limit)

9 g/L (current limit)

=4 times

If we could eliminate the evaporation of active 【HF】, we can use EP acid 4 times more efficiently.
In other words, the cost of EP acid in mass-production become 1/4.

Summary

We have demonstrated the measurement of HF concentration in the EP acid by ICE.

Then we have made five findings.

1.We are loosing 25% HF in the EP acid during making EP acid.

2.We are losing another 33% HF by gas exhaustion during EP process.

3.The dissolved Nb of 9 g/L is still OK.

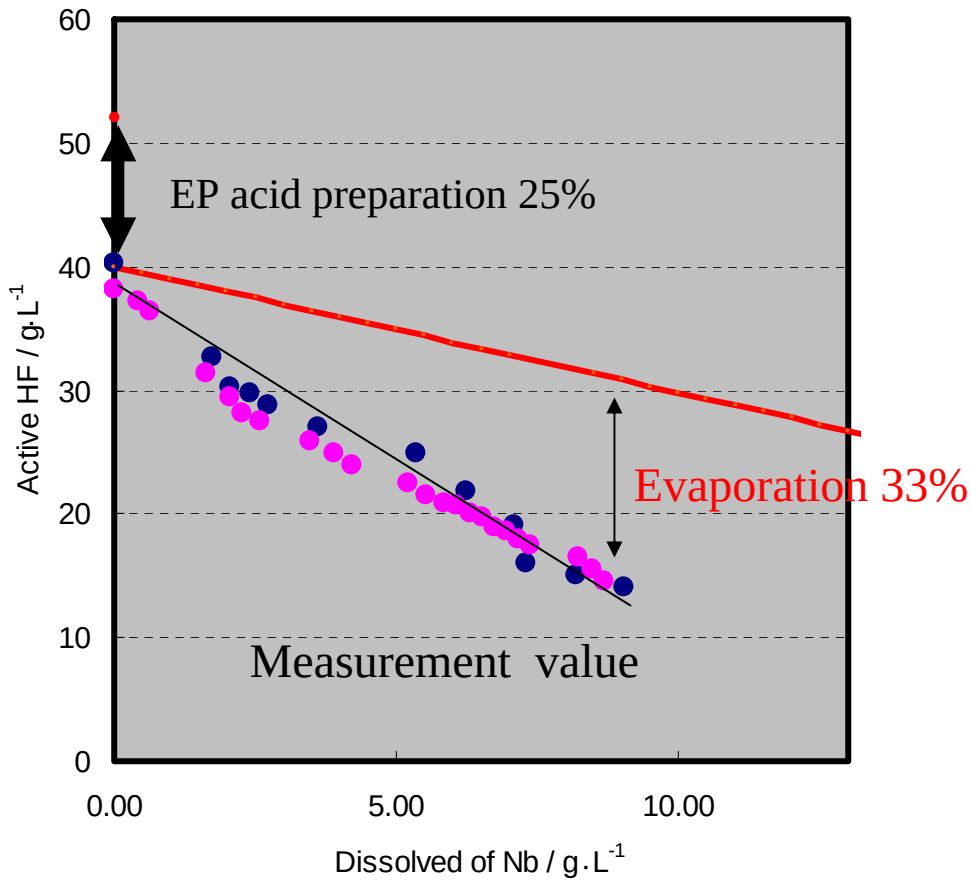
4.HF concentration of 15g/L is OK.

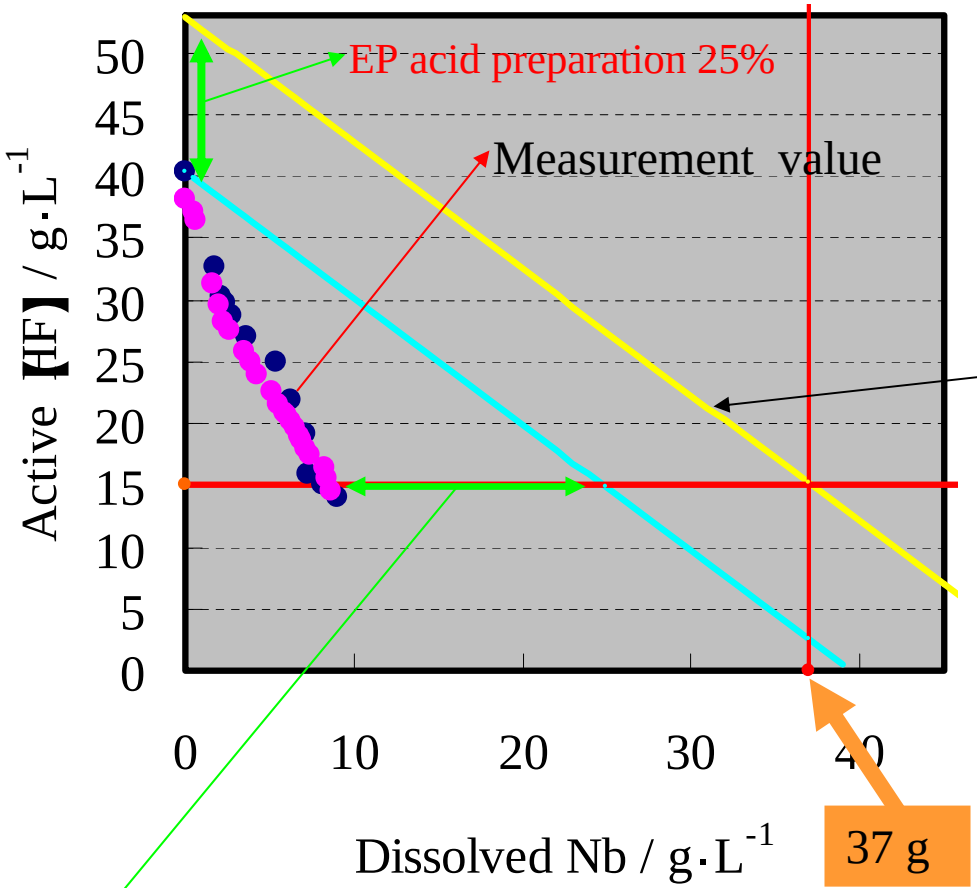
5. If we could stop the evaporations (25%+33%), the EP acid life can be extended four times longer.

Thank you

Thank you

Thank you!


60
50
40
30
20
10
0
Active HF / g·L-1
EP acid preparation 25%
Evaporation 33%
Measurement value
0.00
5.00
10.00
Dissolved of Nb / g·L-1



We assumed that all dissolved Nb in EP acid might form NbF_5.

We also assumed that active 【HF】 is the 【F^-】 which does not form NbF_5 and can be used for additional EP process .

Active 【HF (g/L)】 = 【F-(g/L)】 - 5 ×(19.0/92.9) × 【Nb^{5+}(g/L)】

= 【F-(g/L)】 - 1.02 × 【Nb^{5+}(g/L)】

Evaporation 33%

Evaporation during EP process .

Air flow in EP system?

Analysis of F ion in EP acid

- Junji TAGUCHI (Nomura plating.Co)

Takayuki SAEKI (KEK)

Kenji SAITO (KEK)

2006 September 25 at KEK

Contents

1 We established simple analyzing method of Electropolishing (EP) acid by capillary electrophoresis (CE) measuring system.

2 All ingredients in EP acid were able to be analyzed.

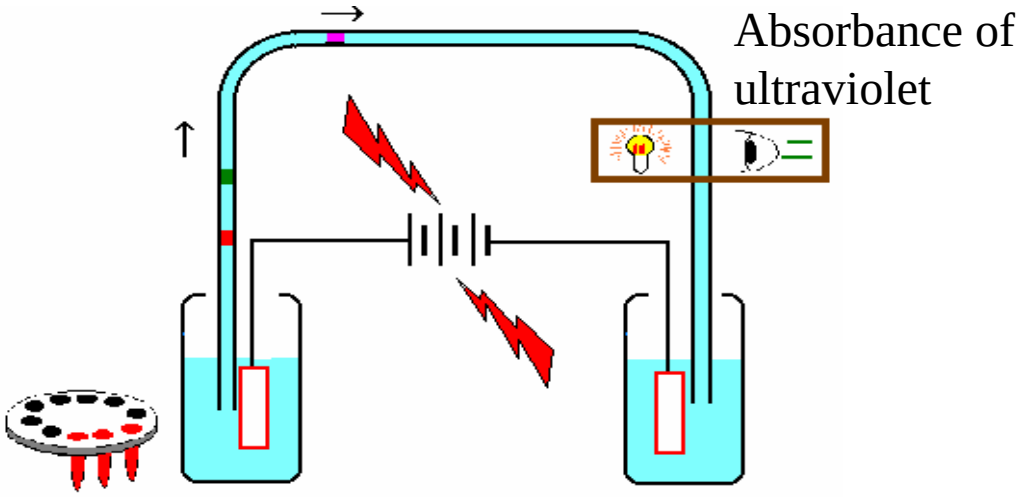
3 【 F^- 】 was constant throughout EP process in KEK laboratory experiment .

4 【 F^- 】 s of 100L, 500L and 1000L tanks decreased after series of cavity EP processes at Nomura plating co,..

Capillary Electrophoresis(CE) measuring system

CAPI-3300 System

Outline figure of C E system



All ingredients in EP acid were measured by capillary electrophoresis (CE) measuring system.

Voltage is applied between both ends of capillary tube. Dissociation occurs according to the difference of adsorption and desorption by any ingredients in a capillary tube. Ingredients are separated by the difference of arriving time at the measuring point of absorbance of ultraviolet.

Calibration

1st step

We bought 1000ppm first standard solutions of NaF, Na_2SO_4 and NbF_5 (Wako pure chem,.)

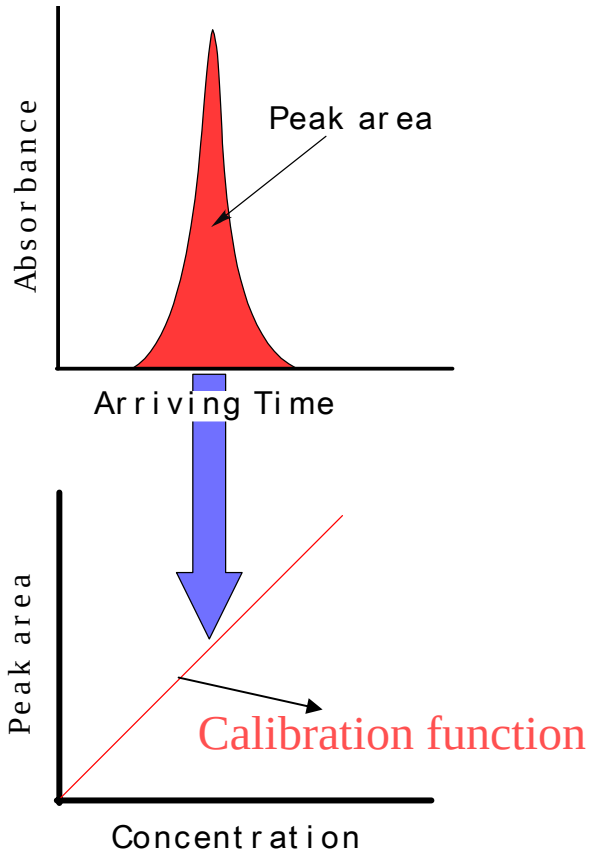
2nd step

In order to make calibration function, we produced three samples of second standard solution for NaF, three samples of second standard solution for Na_2SO_4,and three samples of second standard solution for NbF_5 .

For these nine samples, their peak areas were measured.

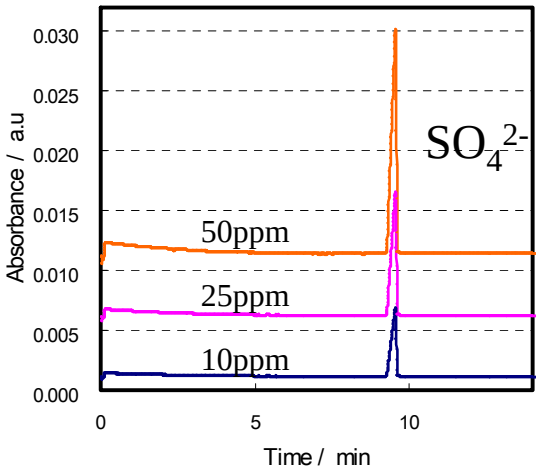
3rd step

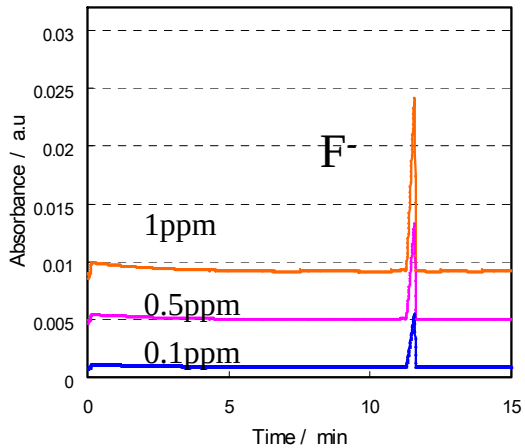
Using known concentration of second standard solutions and measured peak areas, we created calibration functions.

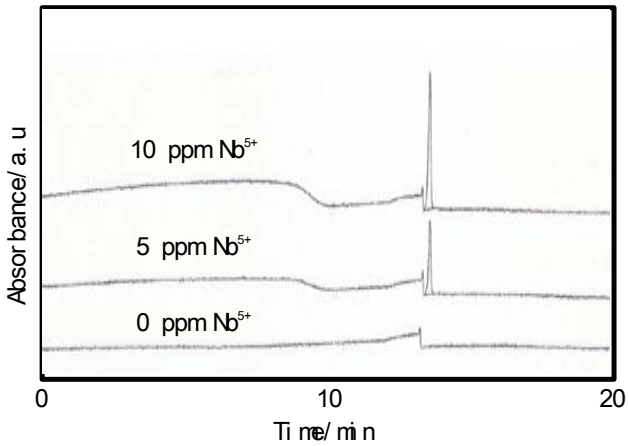


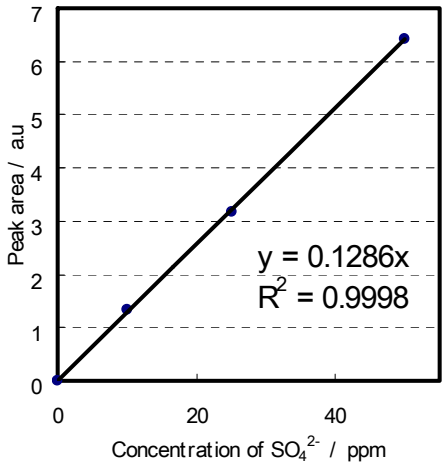
Data taking for calibration (peak area vs concentration)

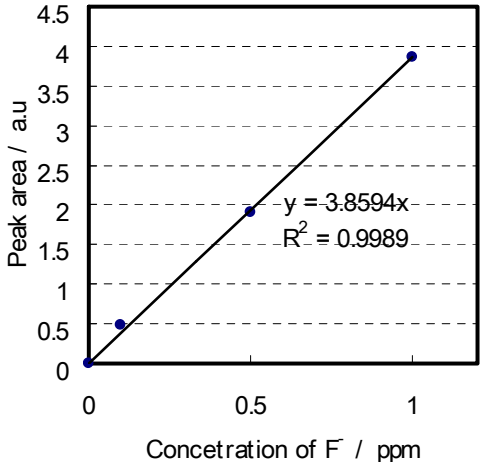
Peak area measurement of SO_4^{2-}, F^- and Nb^{5+} at three different concentrations

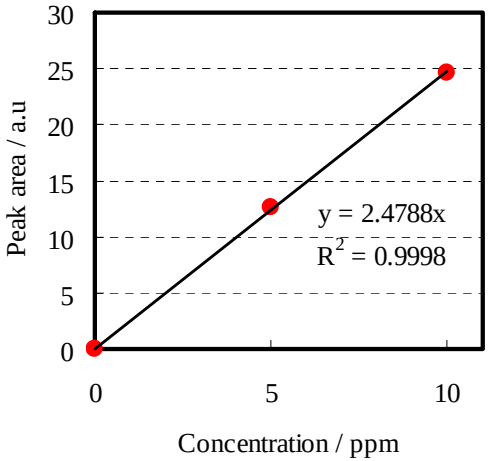








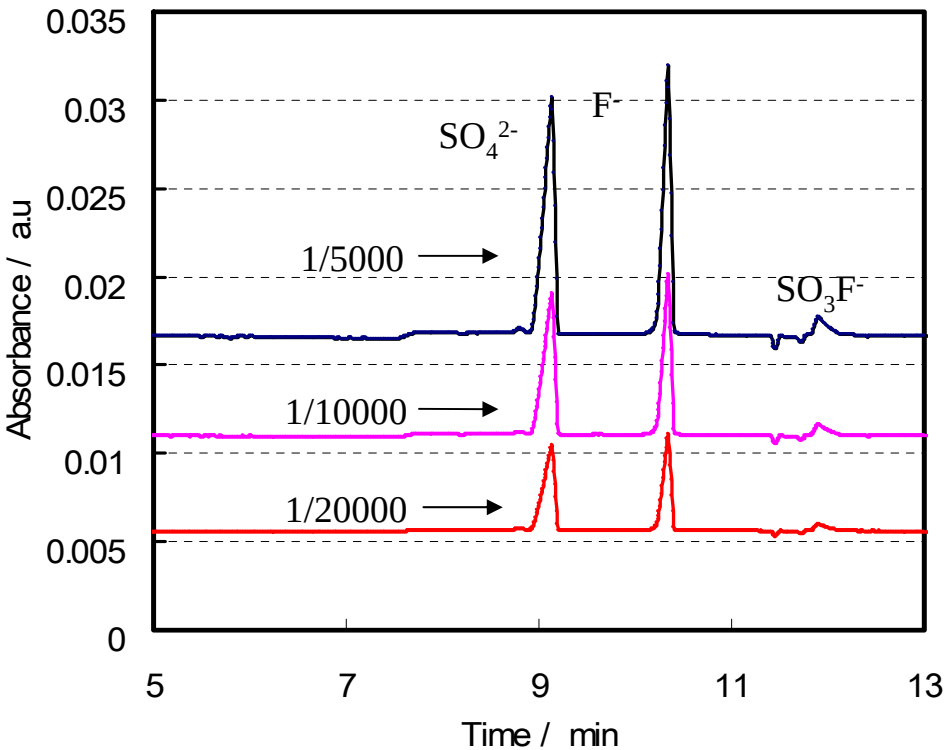




1st experiment

The most important thing is if we could separate SO_4^{2-} , F^- and SO_3F^- in EP acid by CE.

Peaks of SO_4^{2-}, F- and SO_3F^- were successfully separated at three different concentrations



Conditions

HF was added to H_2SO_4. The rate of H_2SO_4 and HF was 9vol : 1vol.

94wt%H_2SO_4 (Wako pure Chem.,)was used, and 46wt%HF (Morita Chem.,) was used.

EP solution was diluted at 1/5000, 1/10000 and 1/20000.

All anions in EP acid were successfully separated.

By measuring peak areas of F^- and SO_4^{2-} and using calibration function ,we obtained concentration of F^- and SO_4^{2-} .

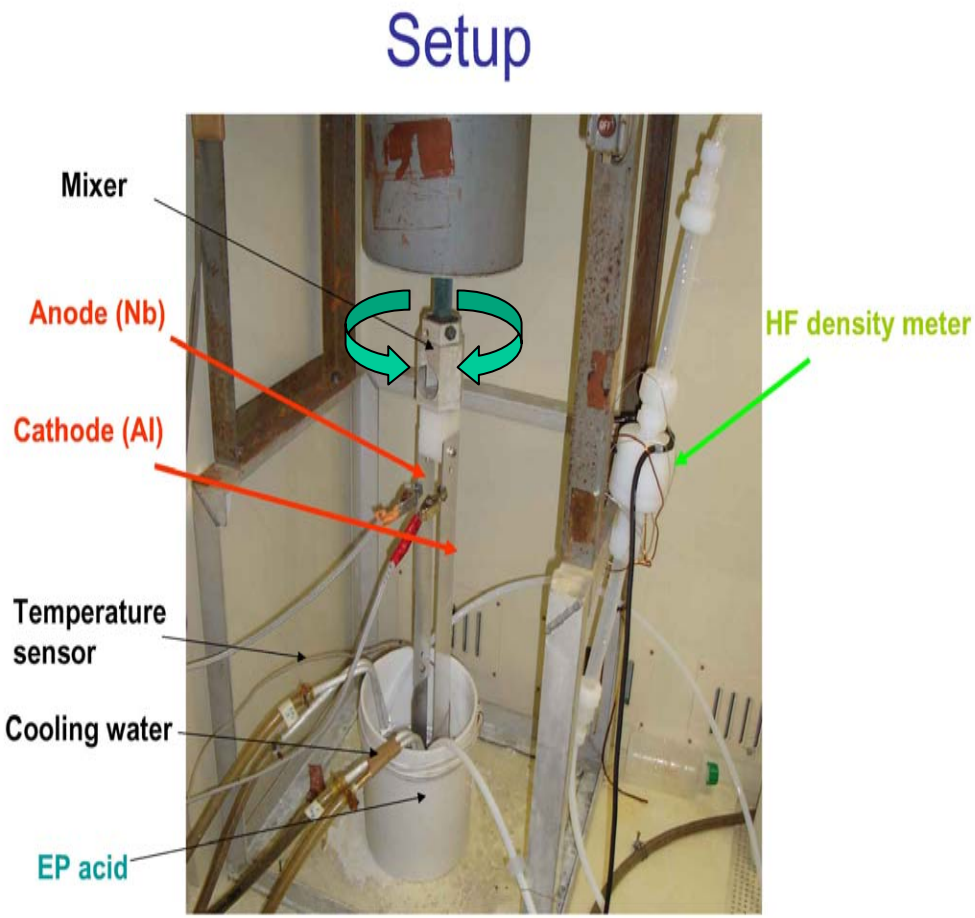
Measured concentrations for F^- and SO_4^{2-} are consistent with expected concentrations.

2nd experiment in KEK laboratory

1st step
EP solution was prepared by mixing 400ml HF and 4000ml H_2SO_4.

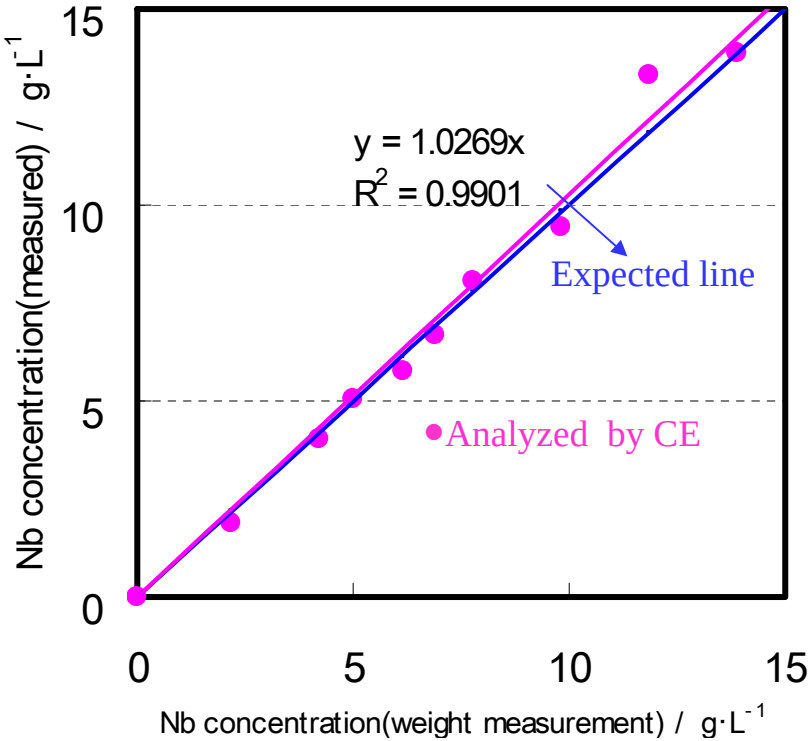
2nd step
Nb-plate (anode) was electropolished in this EP acid.
30 ml of EP acid was sampled at each Nb-concentration of 2 g/L ,4 g/L ,5 g/L ,6 g/L ,7 g/L ,8 g/L 10g/L, 12g/L ,14g/L and 16 g/L.

3rd step
Concentrations of Nb^{5+}, SO_4^{2-} and F^- in EP acid samples were measured by CE measuring system .



Results (Nb^{5+})

Nb^{5+} concentration measurement by CE



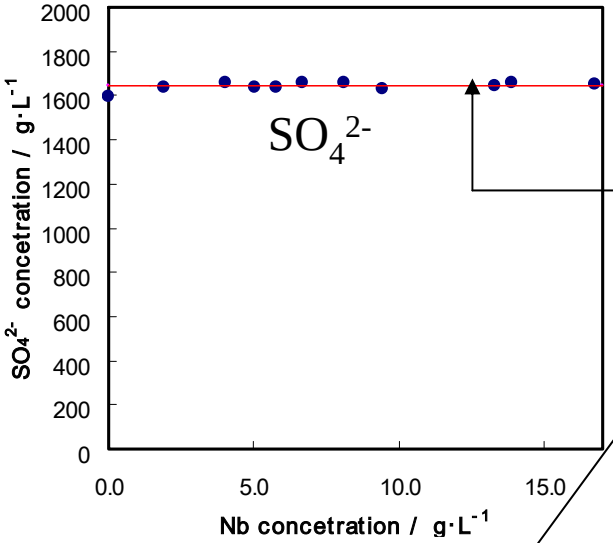
(-●-) is measured concentration by CE.

A horizontal axis is the concentration determined from weight measurement of Nb-plate (Nb anode) .

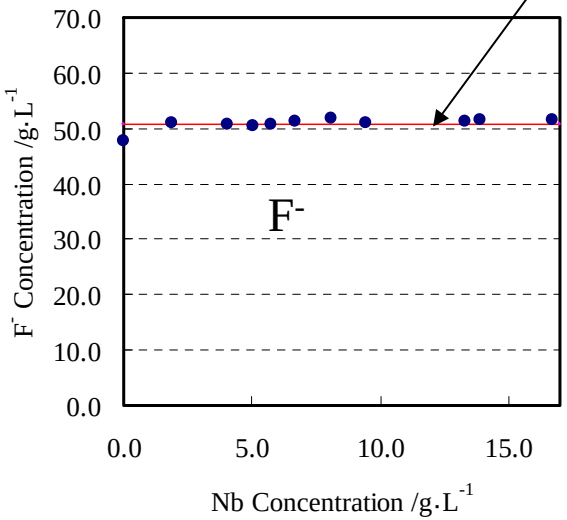
Analyzed concentration by CE are in good agreement with the concentration determined from weight measurement of Nb-plate.

Results (SO_4^{2-}, F^- and active HF)

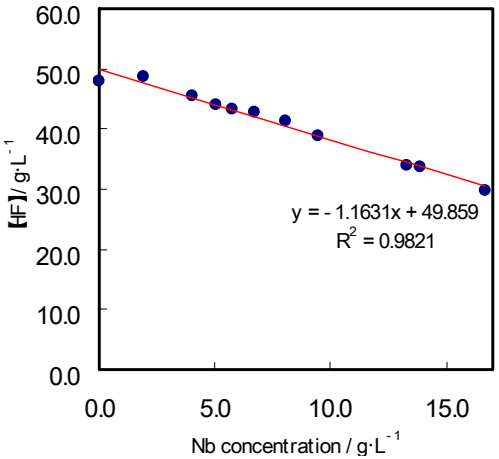
Do the concentrations of SO_4^{2-} and F^- change during the EP process ?



The concentration of SO_4^{2-} and F^- were constant throughout the EP process.



We calculated the concentration of active 【 HF 】



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We also assumed that active 【 HF 】 which can be used for EP process is the 【 F^- 】 which does not form NbF_5 .

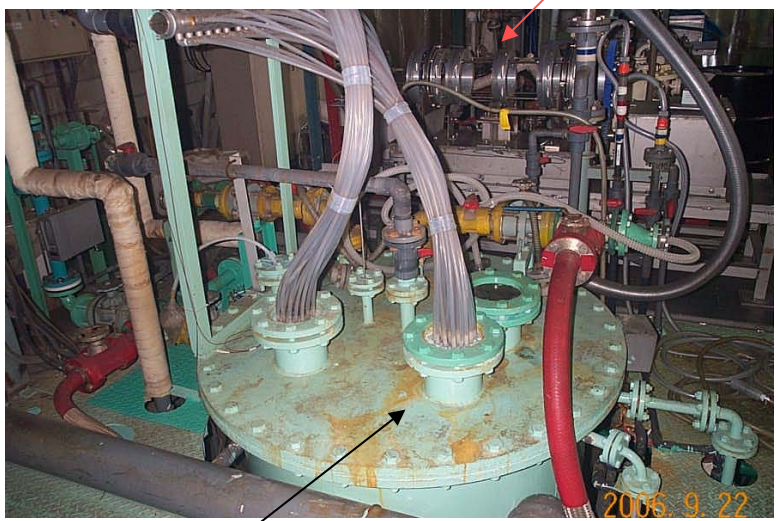
Active 【HF (g/L)】 = 【F-(g/L)】 - 5 ×(19.0/92.9) × 【 Nb^{5+}(g/L)】

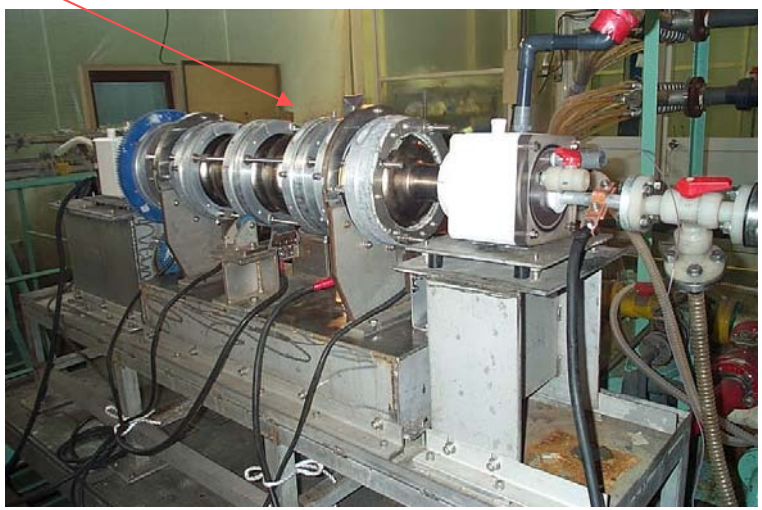
= 【F-(g/L)】 - 1.02 × 【 Nb^{5+}(g/L)】

3rd experiment at Nomura plating co,.

After each EP process of cavity at Nomura plating Co,., F^- in the EP acid was measured by CE.
EP systems are shown blow.

Cavity polishing system



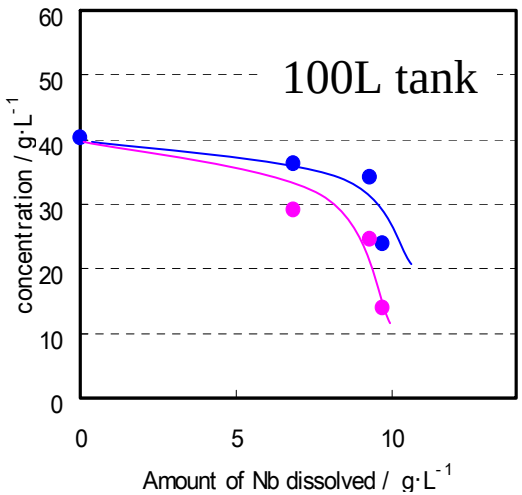


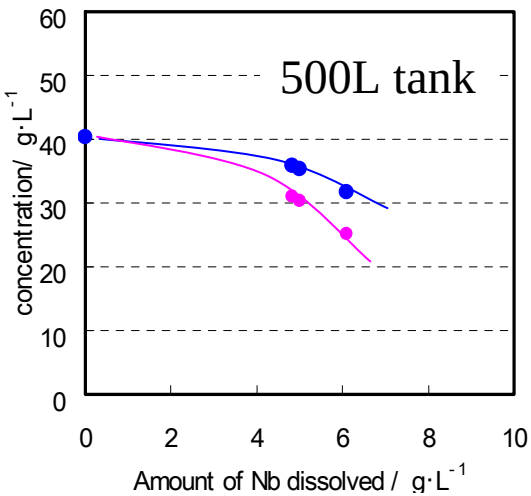
1000 L
Reservoir tank

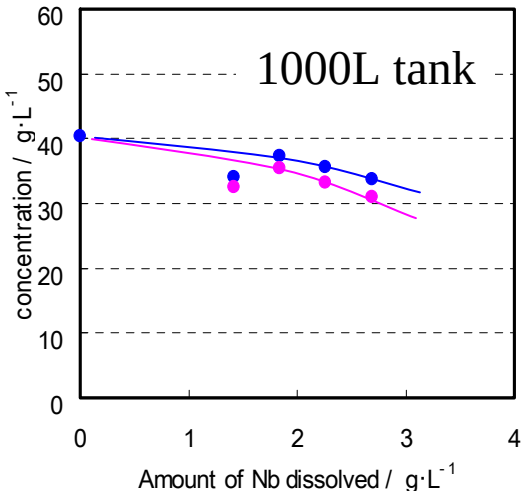
We have three reservoir tanks, 100 L tank for single-cell cavity EP system, 500 L and 1000 L tanks for nine-cell cavity EP system.

Results

We measured the concentration of F^- in each tank and calculated the concentration of active【HF】.







-●- : 【F^-】

-●- : Active【HF (g/L)】= 【F^-(g/L)】 - 1.02 × 【Nb^{5+}(g/L)】

Concentration of F^- decreased. This result is different from the result of 2nd experiment at KEK laboratory. We are considering the reason why these two different results come out.

Conclusion

- We have established simple analyzing method of EP acid by CE.
- All ingredients in EP acid were able to be analyzed.
- We can observe the consumption of active F^- in EP acid by CE.

  And we established a method to monitor consumption of active F^- .

  We will continue the R&D of this monitoring method

Example

- 【 F^- 】 was constant throughout EP process in KEK laboratory experiment .
- 【 F^- 】 s of 100L, 500L and 1000L tanks decreased after series of cavity EP processes at Nomura plating co,..

Ion Capillary Electrophoresis (ICE) measurement system.

CAPI-3300 System

Outline figure of ICE system