LONG-TERM MONITORING OF 3RD-PERIOD EP-ELECTROLYTE IN STF-EP FACILITY AT KEK

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INTRODUCTION

The electro-polishing (EP) facilities in KEK were completed at STF (Super conducting RF Test Facility) area in Dec, 2007. And we have begun to operate in Jan, 2008.
In this facility, the capacity of the electrolyte reservoir tank is 2,000 L (Figure 1).
It is very large. We fill the EP-electrolyte of 2,000kg (≒ 1,100L) into this tank .
And we use it repeatedly many times. The laboratory doing such a usage is only here .
We change the EP-electrolyte three times until now.
And we use the 4th-period EP-electrolyte now.

The electrolyte chemical composition changes with using it repeatedly.
And it gives a big influences to EP-processes.
Therefore its monitoring is very important.
We report the 3rd-period EP- electrolyte monitoring result and the change of chemical composition.
And we suggest the new EP equation from the long period monitoring result until now.

Figure 1 Reservoir tank (2,000L)

THE HISTORY OF THE 3rd-PERIOD EP-ELECTROLYTE.

The beginning use : July.21, 2010
The disposal: July.04, 2011
The using period: about 1 year
The number of times of EP:43 times (Figure 2)
Total removal volume : 13,032g-Nb (Figure 3)

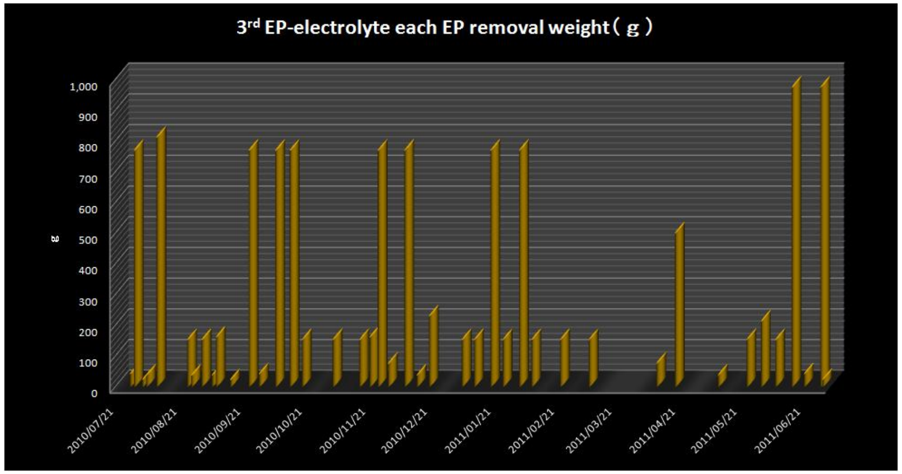


Figure 2:Each removal weight of niobium from cavity for the 43 EP-processes.

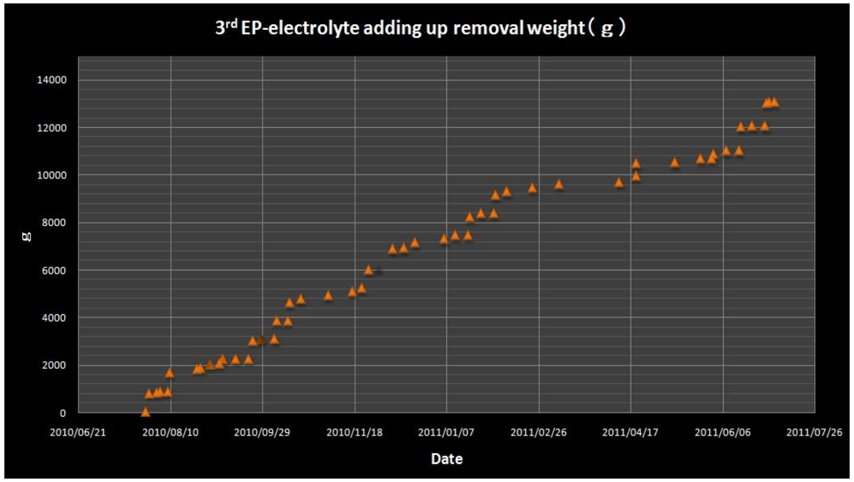


Figure 3:The accumulated removal weight of niobium calculated from the total charge (integrated current) of EP processes vs. date.

RERIODICAL MEASUREMENT OF NIOBIUM CONCENTRATION IN EP-ELECTROLYTE.

Figure 4 is the change of niobium concentration of 3rd-period EP-electrolyte.

At the disposal, the niobium concentration was 12(g/L).

In the 2nd-period EP-electrolyte, it was 9.8(g/L).

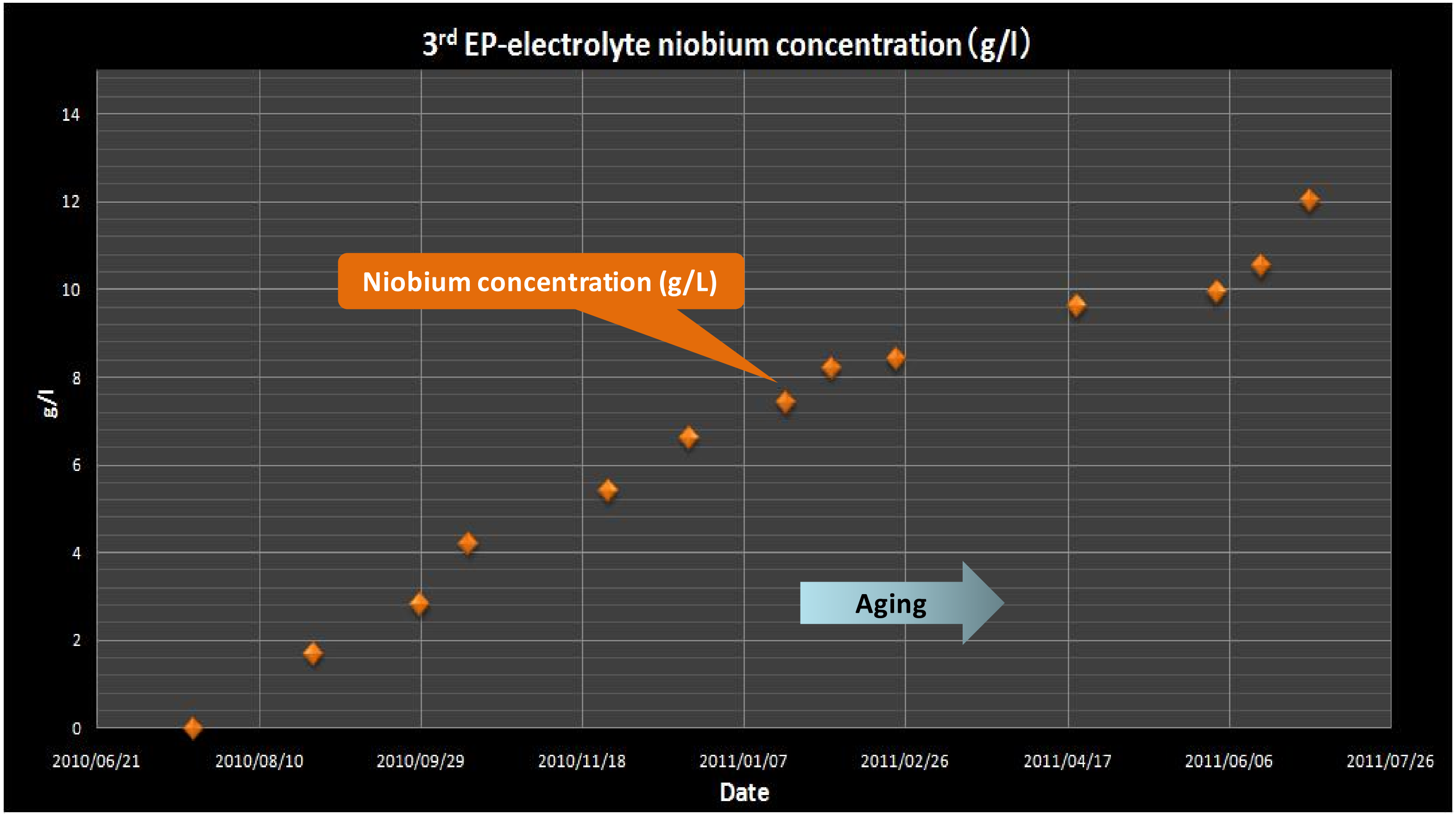


Figure 4:Periodical measurement of niobium concentration by ICP in the 3rd-period EP-electrolyte.

ANALYSIS METHOD OF THE FLUORINE IN THE EP-ELECTROLYTE.

Figure 5 is the ion chromatograph of diluted new EP-electrolyte.

EP-electrolyte hydrolyzes to a fluoride ion(F^-), a sulfate ion(SO_4^{2-}), and a fluorosulfate ion(SO_3F^-).

But in the measurement of fluorine, We can measure only the fluoride ion by ISE (Ion Selective Electrodes) method.

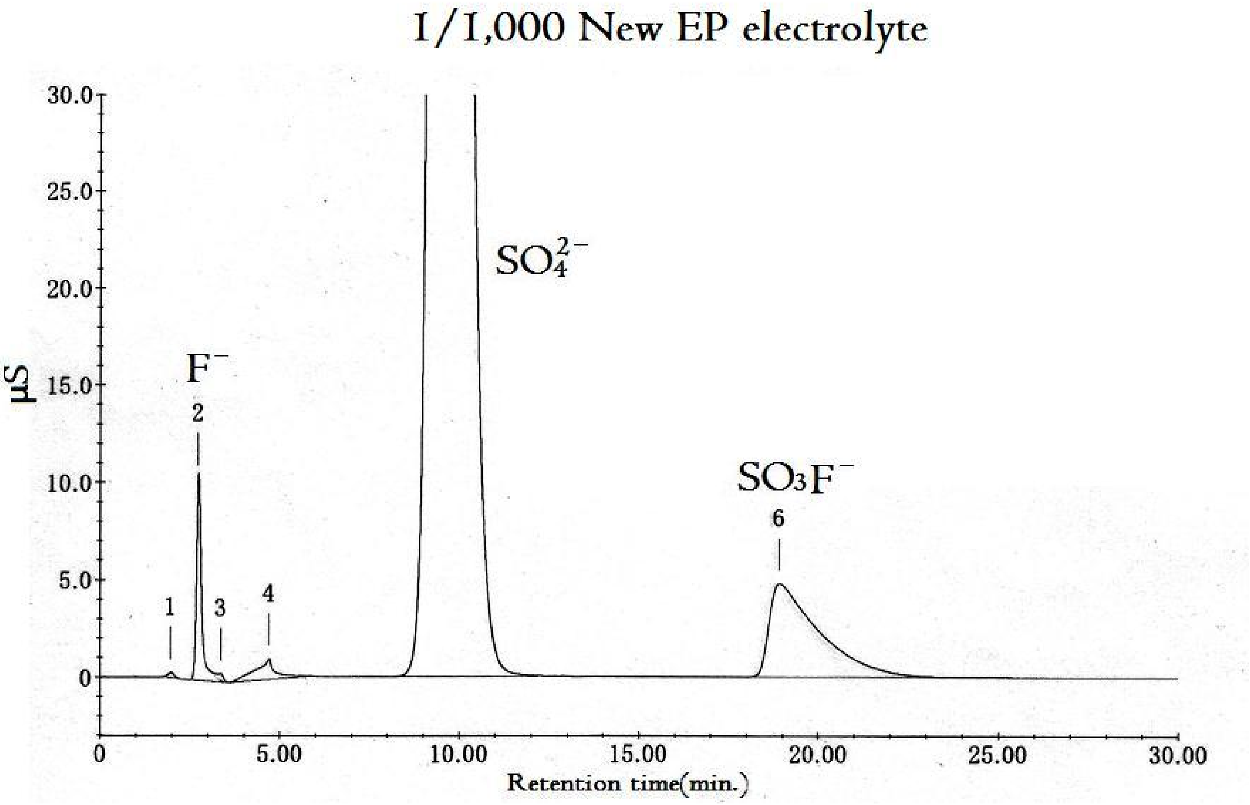


Figure 5: Ion chromatograph of 1/1,000 diluted new EP-electrolyte .

We measure fluorine concentration by the following two ways.

1/500 dilution(n=3)

Direct

The measurement by ISE method

Fluoride ion concentration (as HF)

The steam distillation

The measurement by ISE method

Total fluorine concentration (as HF, FSO_3H ,$HNbF_6$)

The niobium fluorine complex (NbF_6^-) is included in the using EP-electrolyte.

The fluorine concentration in NbF_6^- is calculated by niobium concentration.

The fluorine concentration in $NbF_6^- \fallingdotseq 1.2 \times$ niobium concentration .

In this way, we could measure fluorine chemical species concentration as F^-, SO_3F^-, NbF_6^-.

We call F^- and SO_3F^- "The effective fluorine".

By the way, in the past EP equation, the dissolution of niobium in EP processes was only by HF. There is not the existence of the fluorosulfuric acid.

The past dissolution of niobium.

$$Nb_2O_5 + 6HF \rightarrow H_2NbOF_5(\text{sol.}) + NbO_2F_x\,0.5H_2O(\text{insol.}) + 1.5H_2O$$

$$NbO_2F_x\,0.5H_2O + 4HF \rightarrow H_2NbOF_5 + 1.5H_2O$$

Therefore we want to suggest the following new chemical equation.

SUGGESTION OF THE NEW EP CHEMICAL EQUATION.

- The chemical equilibrium in EP-electrolyte is thought about as follows.

  $H_2SO_4 + HF \rightarrow SO_3F^- + H_3O^+$

  $H_2SO_4 \rightarrow HSO_4^- + H^+$

- The oxidation and dissolution of niobium are thought about as follows.

  $2Nb + 5H_2O \rightarrow Nb_2O_5 + 10H^+ + 10e^-$

  The electrochemical oxidation of niobium at anode

  $Nb_2O_5 + 12SO_3F^- + 7H_2O + 10H^+ \rightarrow 2NbF_6^- + 12H_2SO_4$

  The dissolution by the fluorosulfuric acid

  $Nb_2O_5 + 12F^- + 10H^+ \rightarrow 2NbF_6^- + 5H_2O$

  The dissolution by the hydrofluoric acid

- Side reaction (at high temperature)

  $6Nb(metal) + 5SO_4^{2-} + 40H^+ + 36F^- \rightarrow 6NbF_6^- + 5S + 20H_2O$

  A surfur is created by this reaction.

By H. Monjyushiro at KEK

RERIODICAL MEASUREMENT OF FLUORINE CONCENTRATION IN EP-ELECTROLYTE

Figure 6 is the change of fluorine concentration of 3rd-period EP-electrolyte.
Total fluorine concentration decreased to about 74% and the effective fluorine concentration decreased about 50% in comparison with the initial fresh EP-electrolyte.

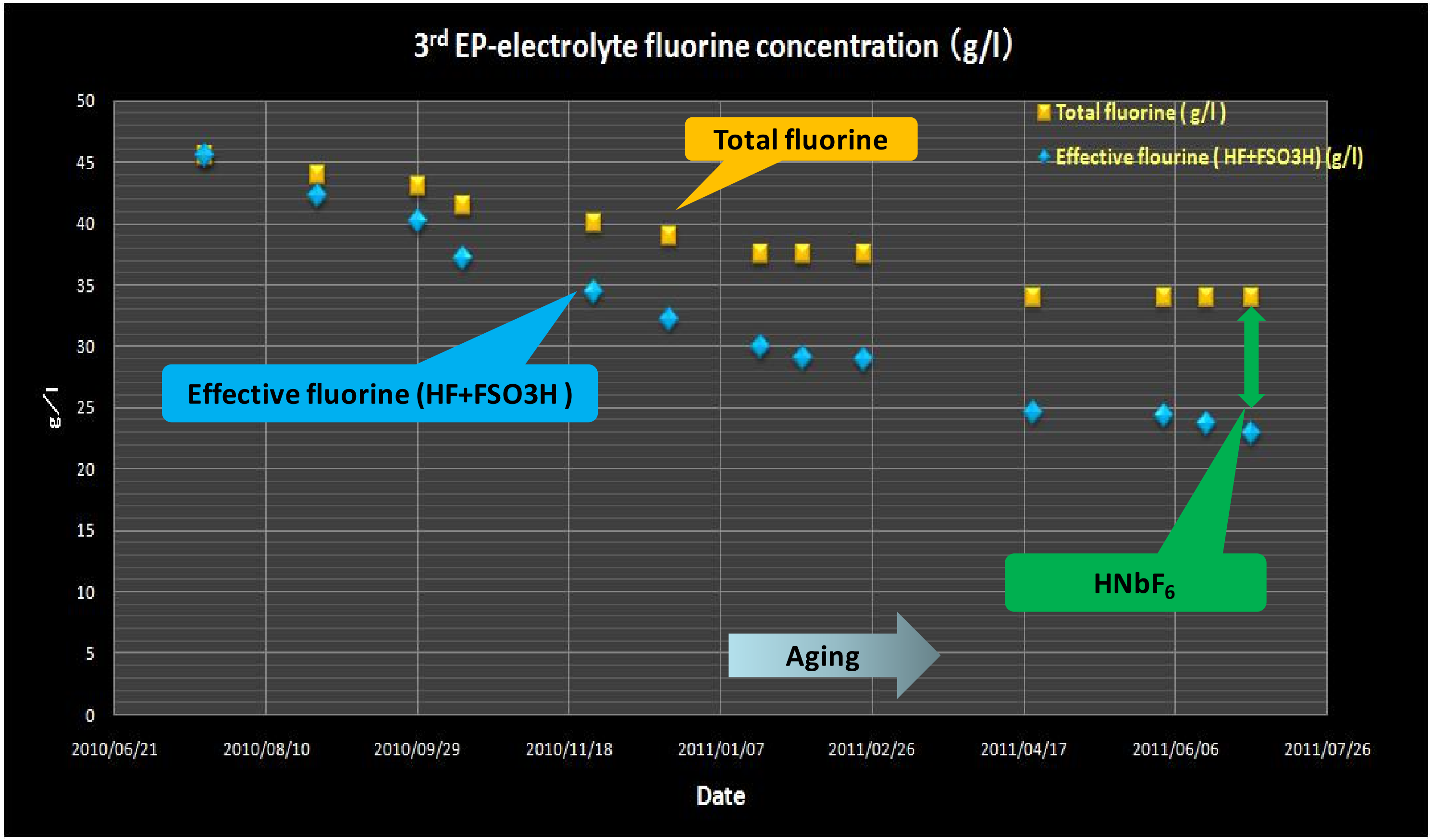


Figure 6: Periodical measurement of the fluorine concentration in the 3rd-reiod EP-electrolyte.

Figure 7 is the result of the 2nd-period EP-electrolyte.
Total fluorine concentration decreased to about 77% and the effective fluorine concentration decreased about 54% in comparison with the initial fresh EP-electrolyte.

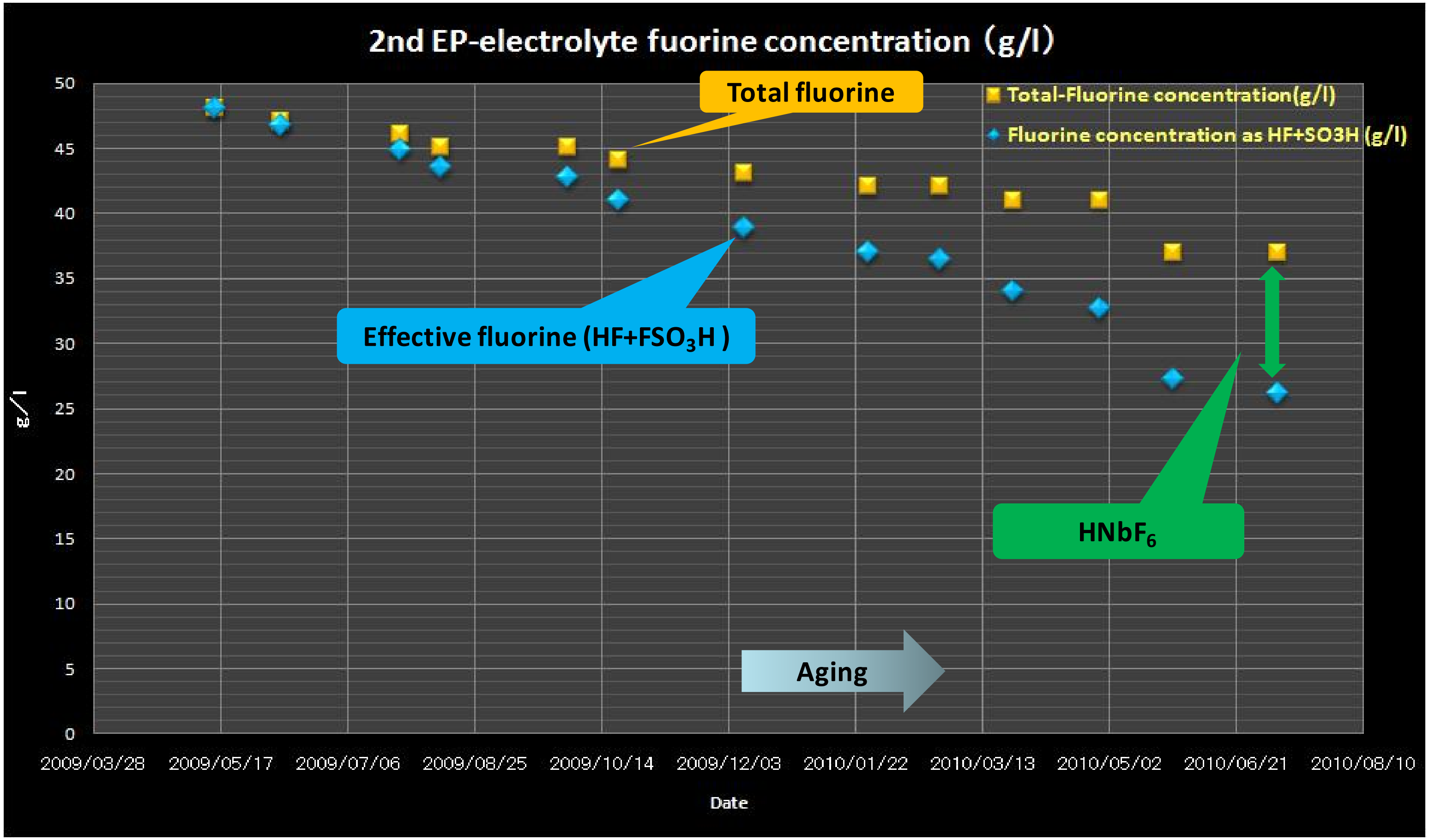


Figure 7: Periodical measurement of the fluorine concentration in the 2nd EP-electrolyte.

Figure 8 is the change of fluorine chemical species concentration in the 1/500 diluted 3rd-period EP-electrolyte.

The fluorosulfate ion (SO_3F^-) decreased by the aging. But the fluoride ion (F^-) increase adversely.

It is thought that hydrolysis of the fluorosulfuric acid advanced by the aging.

In the same way, it is thought that the hydrolysis in the undiluted electrolyte advanced by aging .

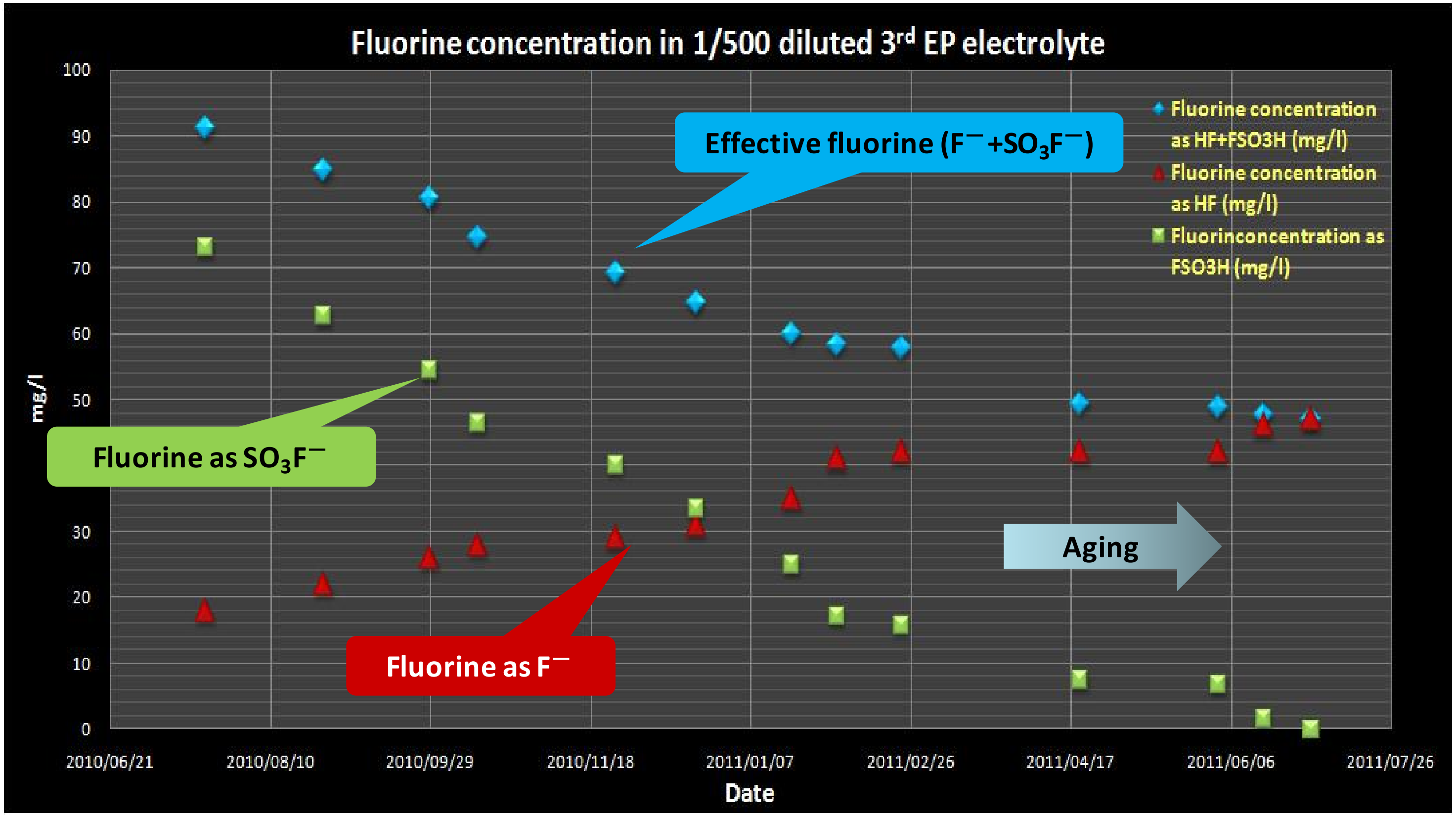


Figure 8: Periodical measurements of the fluorine chemical species concentration in the 1/500 diluted 3rd-period EP-electrolyte vs. date.

Figure 9 is the result of the 1/500 diluted 2nd-period EP-electrolyte.
A similar change is taking place.

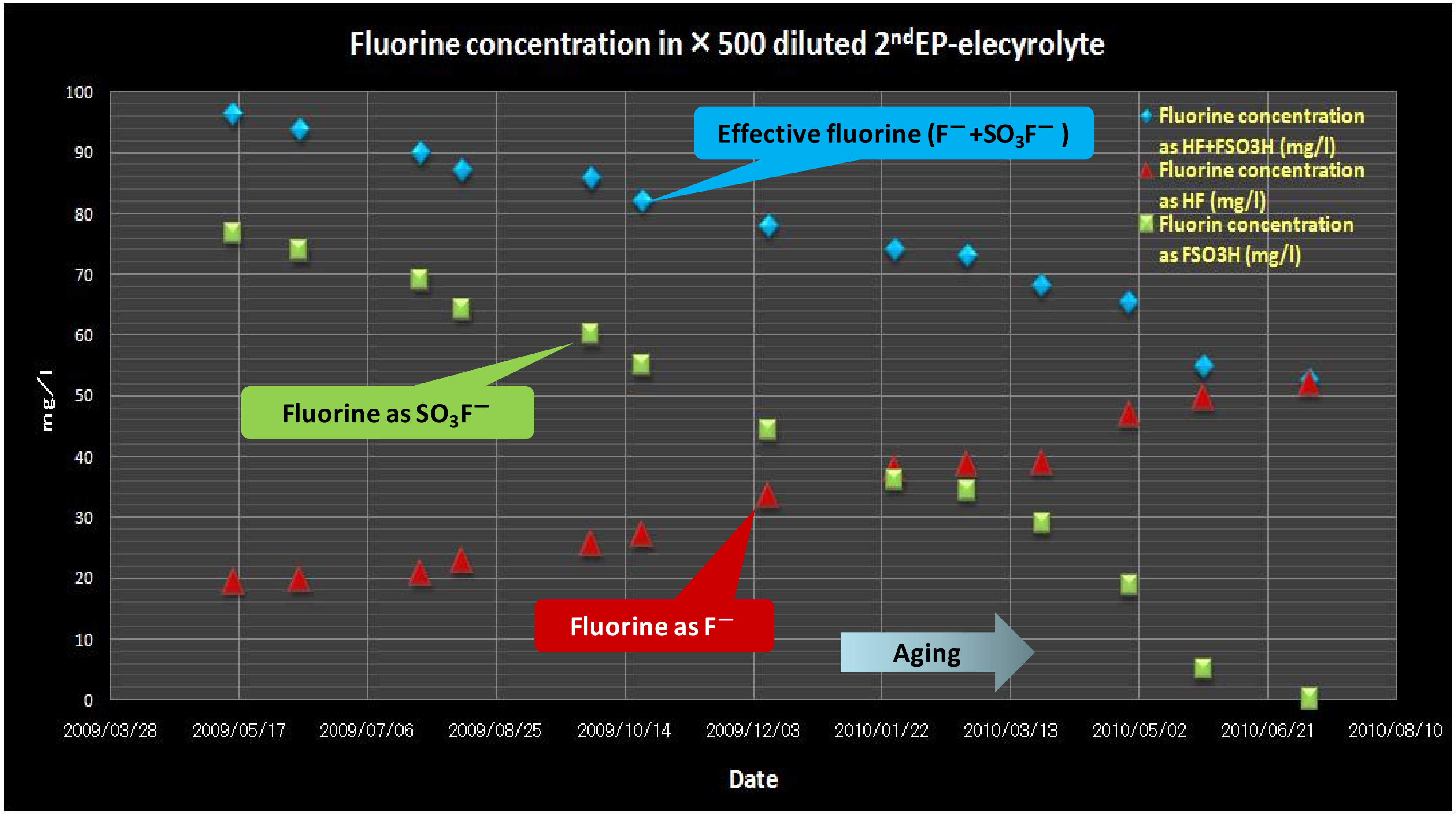
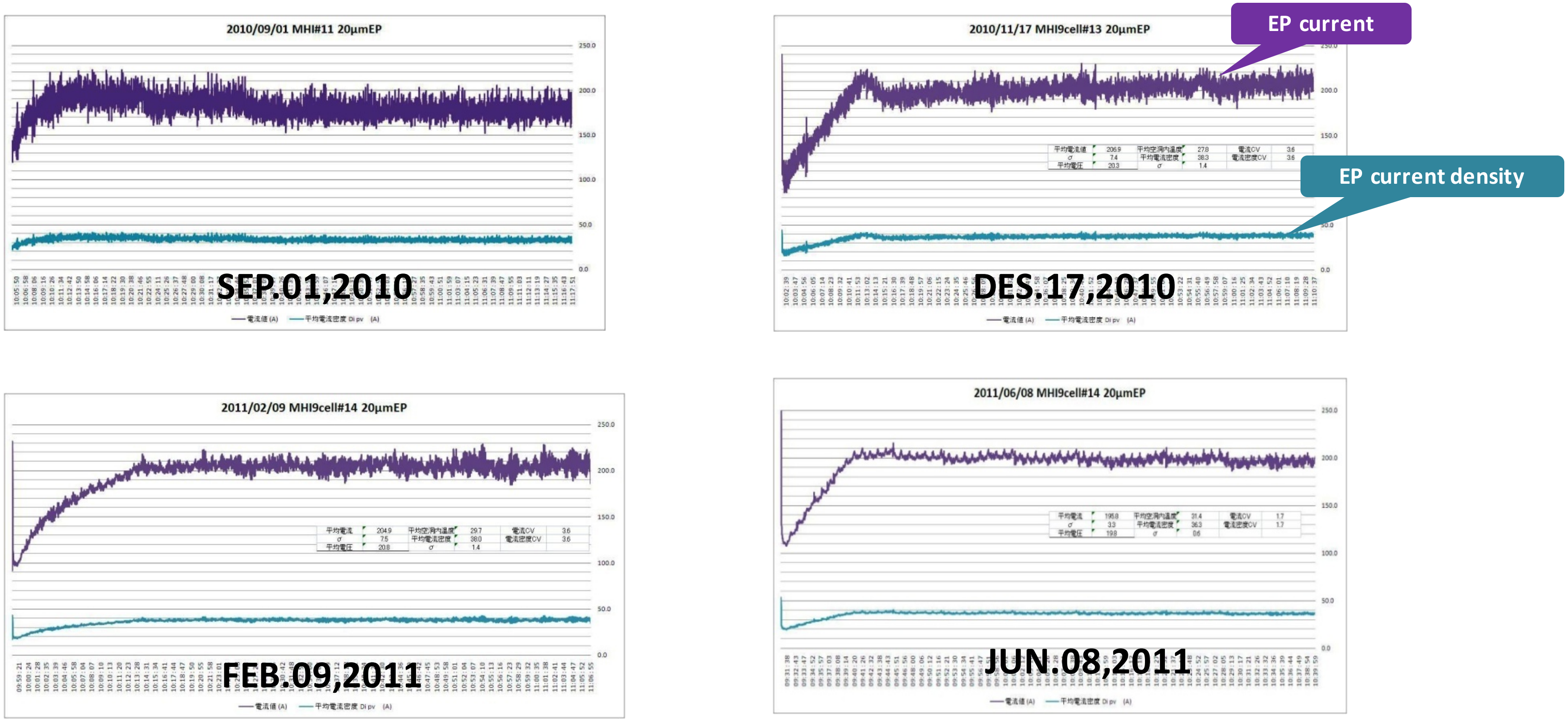


Figure 9: Periodical measurements of the fluorine chemical species concentration in the 1/500 diluted 2nd EP-electrolyte vs. date.

CHANGE OF THE EP ELECTROLYTE COMPOSITION AND EP PROCESS DATA.

Figure 10 is the log data of EP electric current and current density.
The EP-electric current oscillation became small with the aging of EP-electrolyte.
For the digitization of the change, we calculated RSD(%) of the current density which is got every one second and made a graph it.
RSD(%)(Relative Standard Deviation)=σ/Average(%)



平均電流値	206.9	平均空洞内温度	27.8	電流CV	3.6
σ	7.4	平均電流密度	38.3	電流密度CV	3.6
平均電圧	20.3	σ	1.4		

平均電流	204.9	平均空洞内温度	29.7	電流CV	3.6
σ	7.5	平均電流密度	38.0	電流密度CV	3.6
平均電圧	20.8	σ	1.4		

平均電流	195.8	平均空洞内温度	31.4	電流CV	1.7
σ	3.3	平均電流密度	36.3	電流密度CV	1.7
平均電圧	19.8	σ	0.6		

Figure 10: Log datas of current and current density in EP processes.

Figure11 is the superimposed plot of RSD of current density and the niobium concentration vs. date.
Figure12 is the superimposed plot of RSD of current density and $SO_3F^-/(F^-+SO_3F^-)$ ratio vs. date.
It is thought that the change of the EP electric current oscillation is caused of the change of the fluorine chemical species in the EP-electrolyte.
And it is thought that the early dissolution of niobium depends on the fluorosulfuric acid, and gradually depend on the hydrofluoric acid by the EP-electrolyte aging.

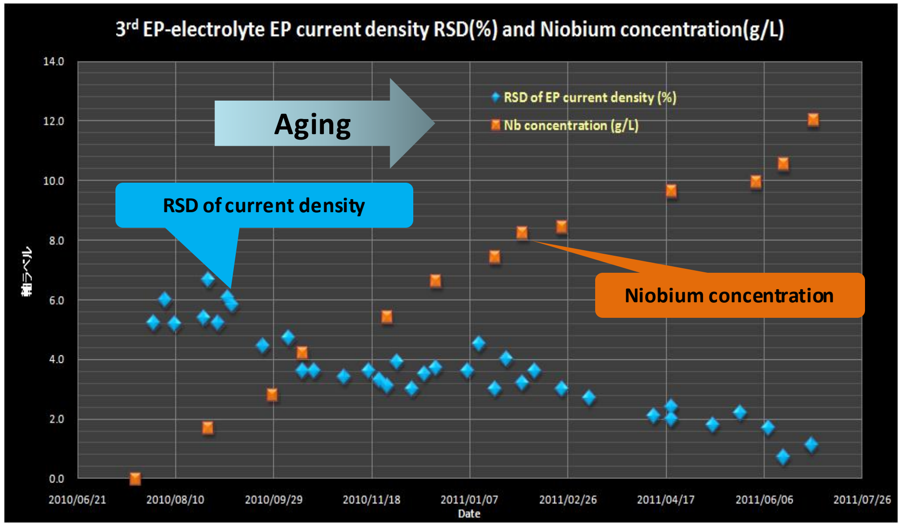


Figure 11:RSD of current density and niobium concentration vs. Date.

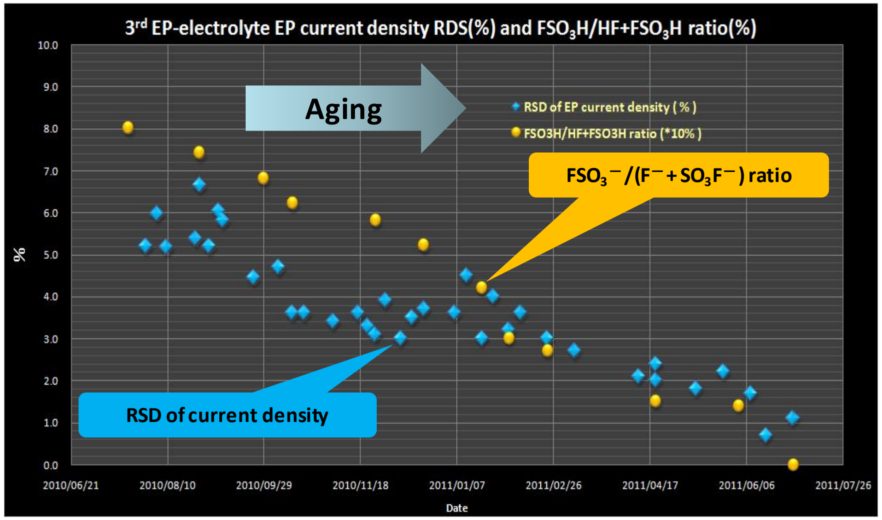


Figure 12:RSD of current density and $FSO_3^-/(F^-+FSO_3^-)$ ratio vs. Date.

In the EP2 (fine EP), we almost electro-polished cavities at current density 30-40mA/cm2 in the 3rd -period EP-electrolyte.

Figure 13 is the correlation between the EP-current density and the EP-voltage in this period.

The change of correlation was not seen by the aging.

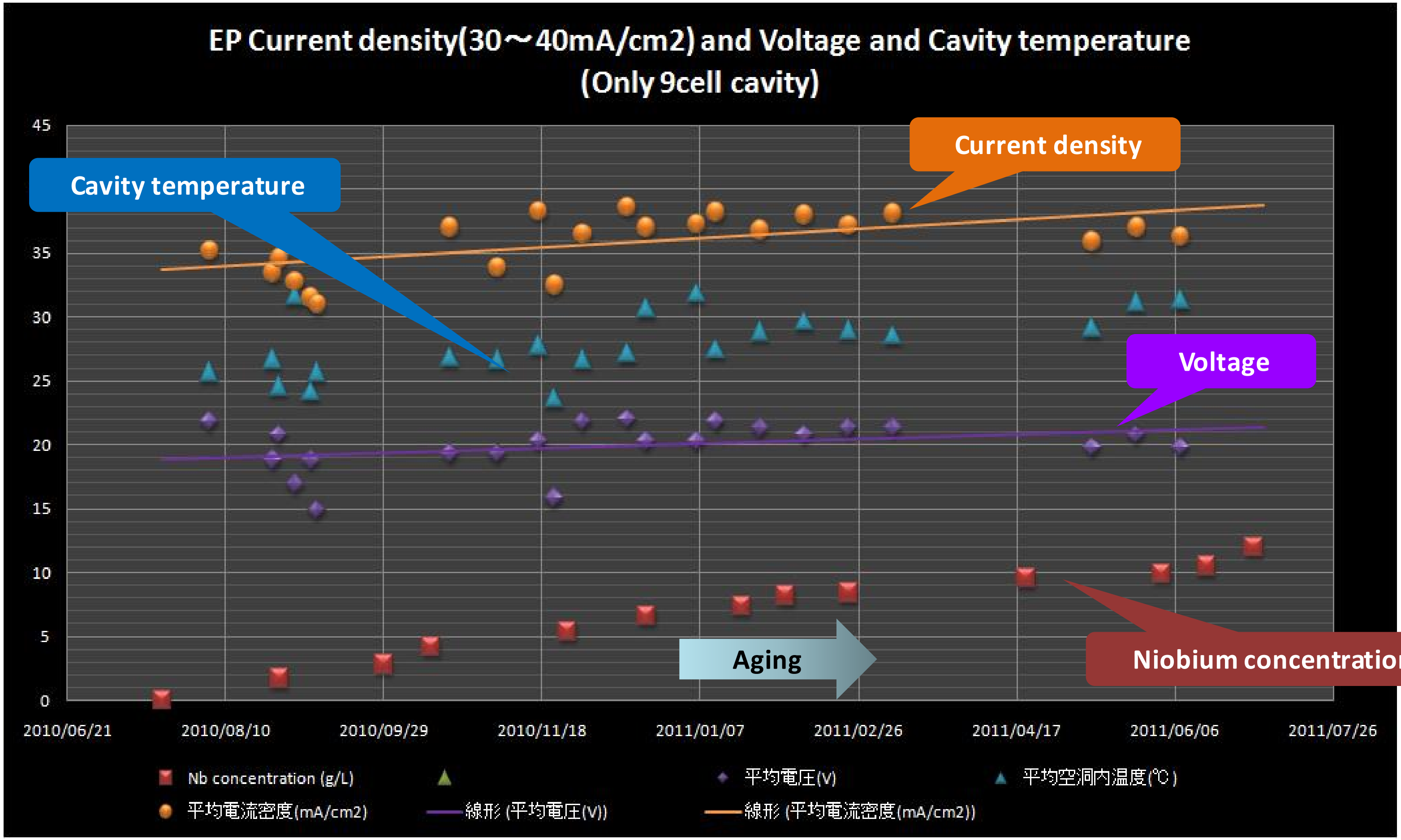


Figure13: The change by the aging of EP current density and voltage and cavity temperature and niobium concentration.(at 30～40mA/cm^2)

In the EP1 (bulk EP), we almost electro-polished cavities at current density 45-50mA/cm2 in the 3rd -period EP-electrolyte.

Figure 14 is the correlation between the EP-current density and the EP-voltage in this period.

The change of correlations was not seen by the aging too.

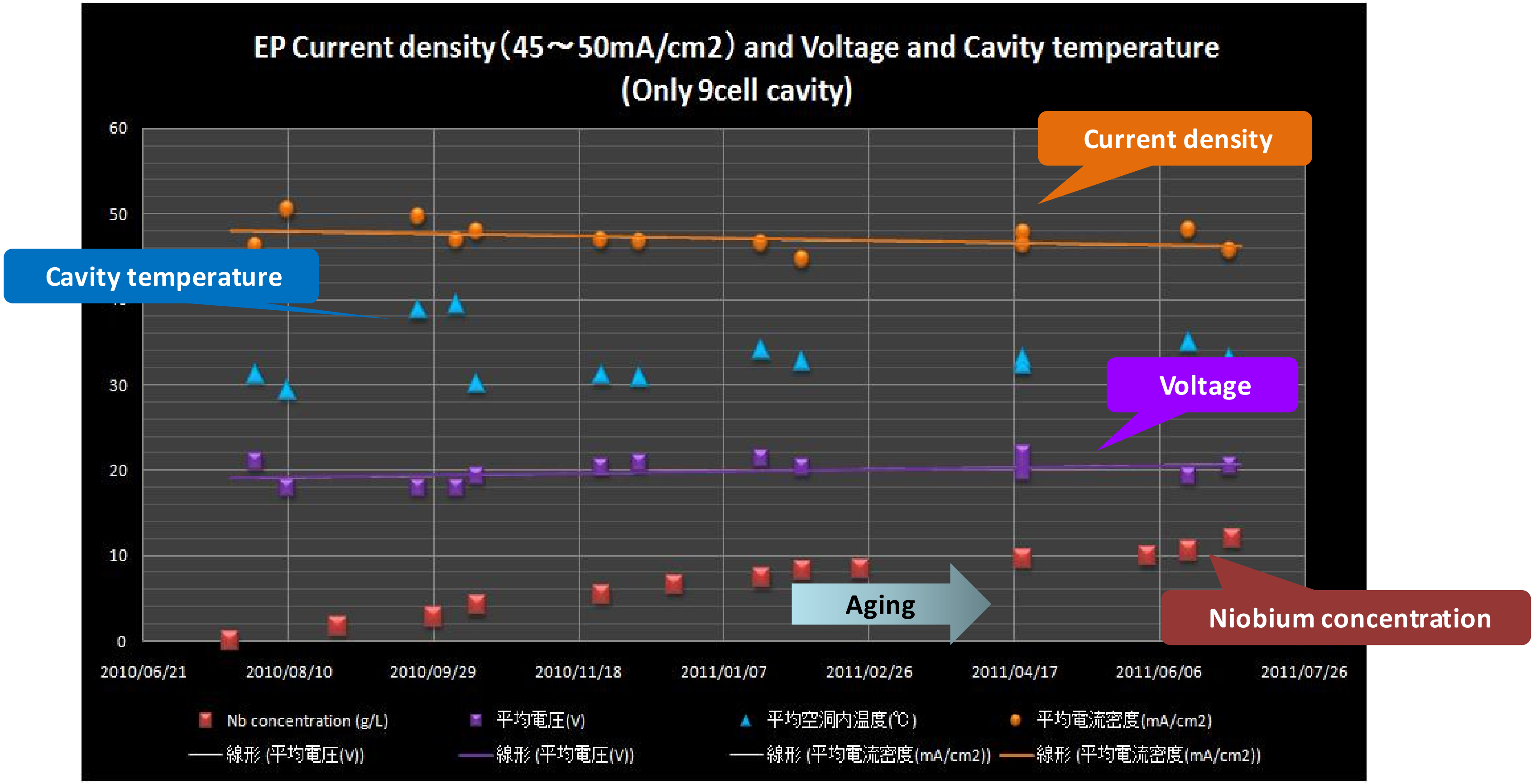


Figure14: The change by the aging of EP current density and voltage and cavity temperature and niobium concentration.(at 45～50mA/cm^2)

THE CAVITY PERFORMANCE RESULTS BY THE 3rd-PERIOD EP-ELECTROLYTE.

Table 1 is the cavity performance results by the 3rd-period EP-electrolyte.
In this electrolyte, we could achieve ILC spec in the four cavities.
We could achieve it by the electrolyte old enough.
At niobium concentration is about 10 g/L.
In thinking about the life (exchange time) of EP-electrolyte, it will be the big result.

Date	Cavity	Performance (MV/m)	Notice
July.28,2010	ERL2cell#2	38.4	
Oct.20,2010	MHI9cell#A	29.1	Non HOM
Nov.04,2010	MHI9cell#12	37.7	
Nov.17,2010	MHI9cell#13	36.4	Achievement of ILC spec.
Des.01,2010	MHI9cell#12	40.7	Achievement of ILC spec.
Des.15,2010	MHI9cell#13	33.1	
May.25,2011	MHI9cell#17	39.2	Achievement of ILC spec.
Jun.08,2011	MHI9cell#14	36.6	Achievement of ILC spec. at niobium concentration about 10g/L
Jun.22,2011	ERL2cell#3	30.3	

Table 1: The cavity performance results by the 3rd-period EP-electrolyte.

SUMMARY

▪In the 3rd-period EP-electrolyte, total fluorine concentration decreased to about 74% and the effective fluorine concentration decreased about 50% in comparison with the initial fresh EP-electrolyte.

▪In the 1/500 diluted EP-electrolyte, the fluorine chemical species changed gradually from fluorosulfate ion (SO_3F^-) to fluoride ion (F^-) by the aging of EP-electrolyte.
It is thought that the hydrolysis of fluorosulfuric acid advanced by the aging.
In the same way, it is thought that the hydrolysis in the undiluted electrolyte advances by the aging.

▪The EP-electric current and current density oscillation became small with the aging.
It is thought that the change of oscillation causes of the fluorine species change by the aging.

▪We want to suggest the new EP equation.
The main point is the dissolution of niobium depends on fluorosulfuric acid and hydrofluoric acid.
And we think that the dissolution product is NbF_6^-.

- The change of correlation between the EP-voltage and the EP-current density is not seen by the 3rd-period EP-electrolyte aging.

- We used the 3rd-period EP-electrolyte until niobium concentration became 12 g/L.
And we could achieve good performance result by the electrolyte old enough.
It will become the big result in thinking about the life (exchange time) of EP-electrolyte.

Thank you very much.