

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

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Abstract

We have constructed an Electro-polishing (EP) Facility in the Superconducting RF Test Facility (STF) at KEK at the end of 2007. We have been operating the EP facility since January 2008 and have performed the EP- processes of cavities about 200 times up to the present. [1, 2]

We changed EP-electrolyte in the 2,000L tank three times until now. And we use the 4th-period EP-electrolyte now. We presented the long-term monitoring result of the 2nd-period EP-electrolyte so far. [3]

In this report, we present the long-term monitoring results of the 3rd-period EP-electrolyte, the correlation between EP-process data and the change of fluorine chemical species by EP-electrolyte aging, the result that we could achieve good performance by the EP-electrolyte old enough.

And we want to suggest the new EP chemical equation.

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 (\cong 1,100L) into this tank, and use it repeatedly many times. The laboratory doing such a usage is only here.

We changed the EP-electrolyte three times until now. The 1st-period EP-electrolyte was used from Jan. 2008 to May 2009. The 2nd-period EP-electrolyte was used from May 2009 to July 2010. And the 3rd-period EP-electrolyte was used July 2010 to July 2011. And we use the 4th-period EP-electrolyte now.

The electrolyte chemical composition changes with using it repeatedly, and gives a big influence 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.

THE HISTORY OF THE 3RD-PERIOD EP-ELECTROLYTE

Table 1 shows the history of the 3rd-period EP-electrolyte. We used this EP-electrolyte for about one year and performed 43 times EP-processes.

Figure 2 shows each removal weight of niobium from cavity, which was calculated from the total charge (integrated current) of each EP-process, for 43 EP-

processes. The accumulated removal weight of niobium from cavities, which was calculated from the total charge (integrated current) of all the EP-processes, was 13,032 g (Figure 3).



Figure 1: Reservoir tank of EP-electrolyte (2,000 L) in STF-EP facility at KEK.

Table 1: 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	EP:43 times
Total removal volume	13,032g-Nb

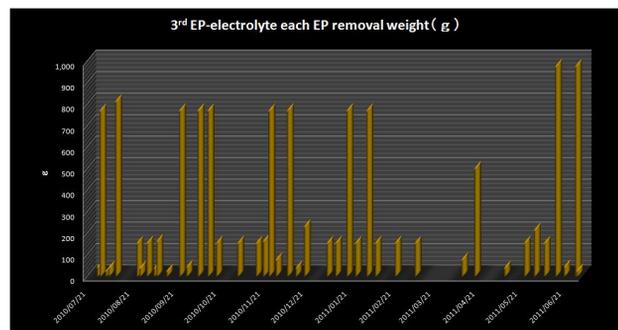


Figure 2: Each removal weight of niobium from cavity for the 43 EP-processes.

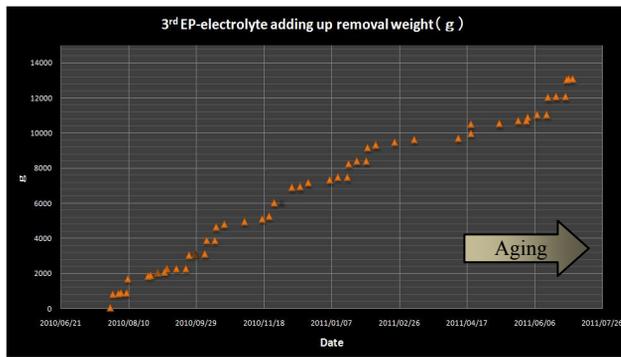


Figure 3: The accumulated removal weight of niobium calculated from the total charge (integrated current) of the 3rd-period EP processes vs. date.

MONITORING RESULTS

Periodical Measurements of Niobium Concentration in EP- electrolyte

Figure 4 shows the result of the periodical measurements of the niobium concentration by ICP in the 3rd-period EP-electrolyte. The niobium concentration at the time of the disposal was 12 (g/L). In the 2nd-period EP-electrolyte, It was 9.8 (g/L) at the time of the disposal. [3]

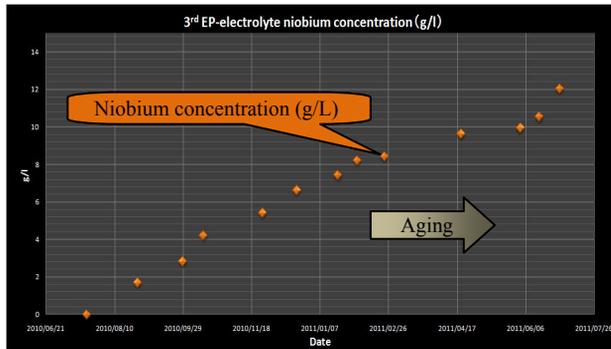


Figure 4: Periodical measurements of niobium concentration by ICP in the 3rd-period EP-electrolyte vs. date.

Periodical Measurements of Fluorine Concentration in EP- electrolyte

Figure 5 shows the result of periodical measurements of the fluorine concentration in the 3rd-period EP-electrolyte. Total fluorine concentration decreased to about 74% and the effective fluorine concentration ($F^- + SO_3F^-$) decreased to about 50% in comparison with the initial fresh EP-electrolyte.

In the 2nd-period EP-electrolyte, total fluorine concentration decreased to about 77% and the effective fluorine concentration ($F^- + SO_3F^-$) decreased to about 54% in comparison with the initial fresh EP-electrolyte. [3]

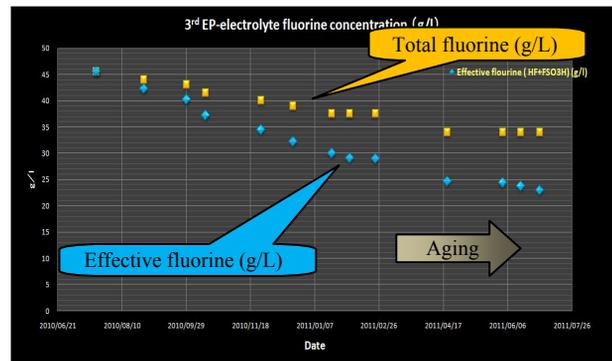


Figure 5: Periodical measurements of fluorine concentration in 3rd-period EP-electrolyte vs. date.

Periodical Measurements of Fluorine Chemical Species Concentration in 1/500 diluted EP - Electrolyte

Figure 6 shows the result of periodical measurements of the fluorine chemical species concentration in 1/500 diluted the 3rd-period EP-electrolyte. The fluorosulfate ion (SO_3F^-) decreased by the aging. But the fluoride ion (F^-) increased adversely. We were able to observe the similar change in the 2nd-period EP-electrolyte. (Figure 7) [3]

It is thought that the hydrolysis of fluorosulfuric acid in undiluted EP-electrolyte advanced by the aging.

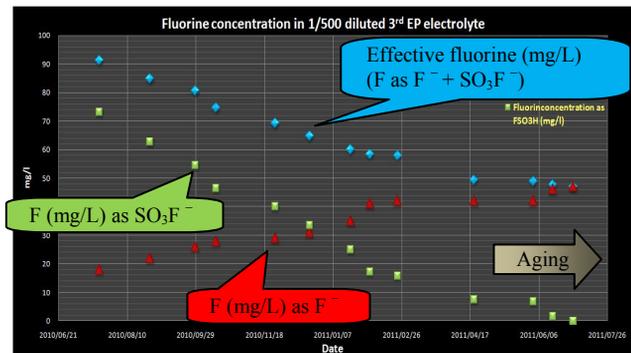


Figure 6: Periodical measurements of the fluorine chemical species concentration in 1/500 diluted the 3rd-period EP-electrolyte vs. date.

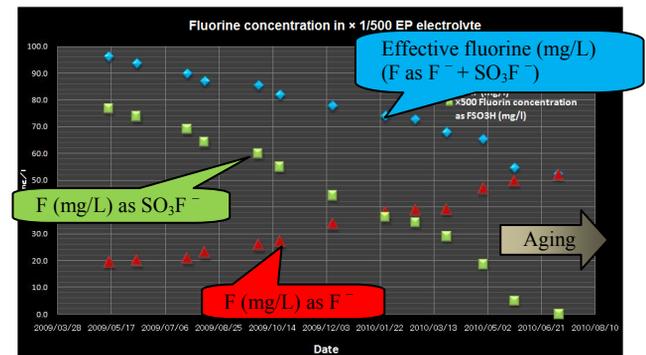


Figure 7: Periodical measurements of the fluorine chemical species concentration in 1/500 diluted the 2nd-period EP-electrolyte vs. date.

CORRELATION BETWEEN EP-PROCESS DATA AND EP-ELECTROLYTE AGING

Figure 8 shows the logging data of current (in the unit of A) and current density (in the unit of mA/cm²) in four EP processes on 1st September 2010, 17th November 2010, 9th February 2011, and 8th Jun 2011, with the 3rd-period EP-electrolyte. The sampling rate of the data was every second. It is seen from the figure that the current oscillation became smaller when the aging of the EP-electrolyte proceeds. We calculated the Relative Standard Deviation (RSD) = Sigma /Average of current density in the unit of % for each EP process for the 3rd-period EP-electrolyte. Figure 9 is the superimposed plot of the RSD of current density and the niobium concentration vs. date for the 3rd-period EP-electrolyte. Figure 10 is the superimposed plot of the RSD of current density and the SO₃F⁻ / (F⁻ + SO₃F⁻) ratio vs. date. It is seen from these figures that there is a correlation between the RDS of current density and the SO₃F⁻ / (F⁻ + SO₃F⁻) ratio.

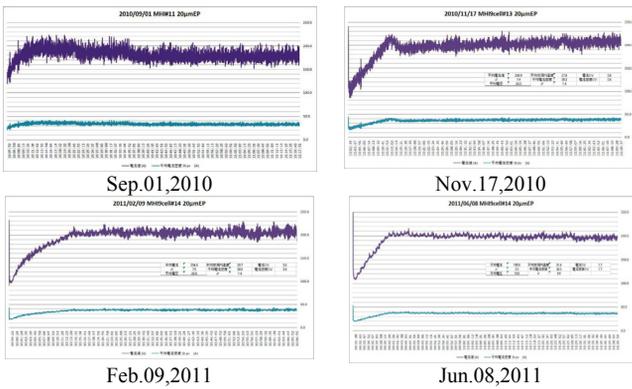


Figure 8: Logging data of current and current density in the 3rd-period EP-electrolyte.

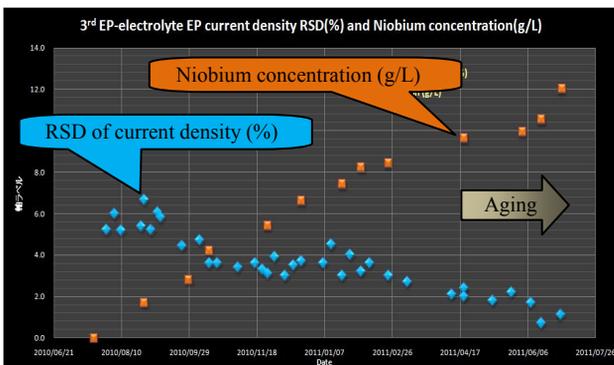


Figure 9: RSD of current density and Nb concentration in the 3rd-period EP-electrolyte vs. date.

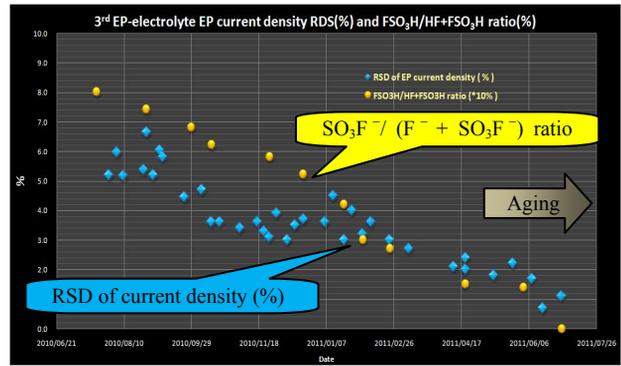


Figure 10: RSD of current density and SO₃F⁻ / (F⁻ + SO₃F⁻) ratio in the 3rd-period EP-electrolyte vs. date.

Changes of the Correlation between EP-voltage and the EP-current Density by the EP-electrolyte Aging

In the case of EP2 (fine EP, about 20 μmEP), we electro-polished cavities at current density 30-40mA/cm² in the 3rd-period EP-electrolyte.

Figure 11 shows the correlation between the EP-current density and the EP-voltage in this period.

The change of correlation was not seen by the EP-electrolyte aging.

In the case of EP1 (coarse EP, about 100 μmEP), we electro-polished cavities at current density 45-50mA/cm² in this period.

Figure 12 shows 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.

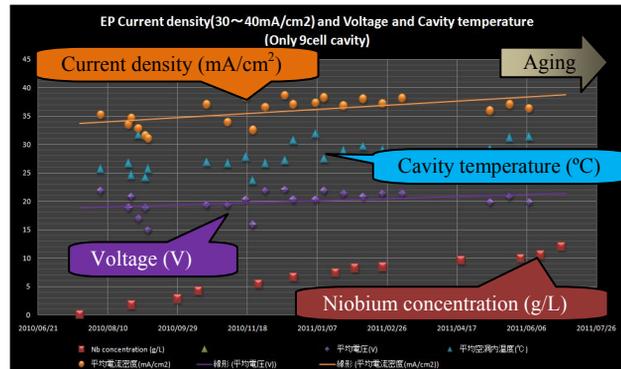


Figure 11: The changes of EP current density and EP voltage and cavity temperature and niobium concentration in the 3rd-period EP-electrolyte vs. date (at 30-40mA/cm²).

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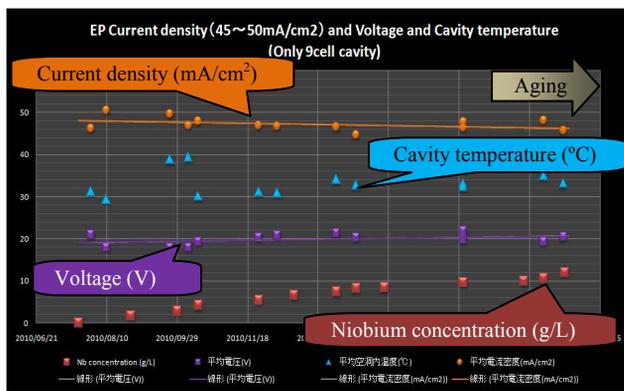


Figure 12: The changes of EP current density and EP voltage and cavity temperature and niobium concentration in the 3rd-period EP-electrolyte vs. date (at 45~50mA/cm²).

THE CAVITIES PERFORMANCE RESULTS BY 3RD-PERIOD EP-ELECTROLYTE

Table 2 shows the cavity performance results by the 3rd-period EP-electrolyte.

We could achieve ILC spec in the four cavities by the 3rd-period EP-electrolyte.

And 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.

Table 2: The Cavities Performance Result by the 3rd-period EP-electrolyte

Date	Cavity	Performance (MV/m)	Notice
Jul.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 ILC spec
Dec.01,2010	MHI9cell#12	40.7	Achievement ILC spec
Dec.15,2010	MHI9cell#13	33.1	
May.25,2011	MHI9cell#17	39.2	Achievement ILC spec
Jun.08,2011	MHI9cell#14	36.6	Achievement ILC spec Niobium concentration about 10g/L.
Jun.22,2011	ERL2cell#3	30.3	

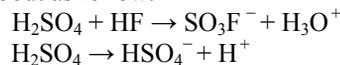
CONSIDERATION

By the long-term monitoring results in the 2nd- and 3rd-period EP-electrolyte, we understood that fluorosulfuric acid and hydrofluoric acid exist as fluorine chemical species in EP-electrolyte and the fluorosulfuric acid is hydrolyzed to hydrofluoric acid by the aging.

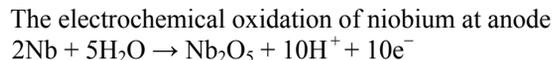
By the way, in the past EP equation, the dissolution of niobium in the EP-processes depends on only the hydrofluoric acid. There is not the existence of fluorosulfuric acid.

Therefore we want to suggest the following new chemical equation of EP-processes.

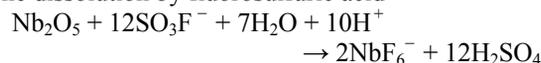
The chemical equilibrium in EP-electrolyte is thought about as follow.



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



The dissolution by fluorosulfuric acid



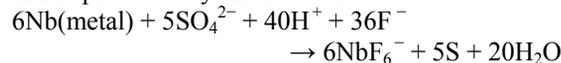
The dissolution by hydrofluoric acid



NbF₆⁻ was detected by Laser Raman spectroscopy method in the used EP-electrolyte.

Side reaction (at high temperature)

Sulfur is produced by this reaction.



Sulfur was produced with niobium powder and new EP-electrolyte by our experiment. The temperature was more than approximately 40-50 degrees Celsius.

We think that the dissolution of niobium depends on the fluorosulfuric acid in the fresh EP-electrolyte and gradually depend on the hydrofluoric acid by the EP-electrolyte aging.

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 (SO₃F⁻) to fluoride ion (F⁻) by the EP-electrolyte aging. It is thought that the hydrolysis of fluorosulfuric acid in the undiluted electrolyte advanced by the EP-electrolyte aging.

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

- We want to suggest the new EP equation. The main point is that 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 was not seen in 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 EP-electrolyte old enough.
- It will become the big result in thinking about the life (exchange time) of EP-electrolyte.

REFERENCES

- [1] M. Sawabe, et al., TTC-Meeting Apr, 2010 “Quality control of KEK STF”.
<https://indico.fnal.gov/conferenceDisplay.py?confId=3000>
- [2] M. Sawabe, et al., Paper ID: WEPEC027, IPAC10, May 2010, “Long-monitoring of Electro-polishing Electrolyte in EP facility at KEK”.
- [3] M. Sawabe, et al., Paper ID: TUPO039, SRF2011, July, 2011, “Long-term monitoring of 2nd-period EP-electrolyte in STF-EP facility at KEK”.