Niobium Powder Production in Molten Salt by Electrochemical Pulverization

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Niobium and Tantalum

Table Comparison of Nb with Ta

	Nb	**Ta**
Atomic number	VB 41	VB 73
Crystal structure	bcc	bcc
Melting point	2468 °C	2980 °C
Density	8.56 g/cm^3	16.65 g/cm^3
Dielectric constant of pentoxide	**41**	**27**
Reserves	4,400,000 ton Nb	43,000 ton Ta
Annual world productivity	23,000 ton Nb	2,300 ton Ta
Price	**~ 50 $/kg**	**~ 700 $/kg**
Major applications	Microalloy element for steel	Solid electrolytic capacitor
Commercial production process	Aluminothermic reduction (ATR)	Sodiothermic reduction (Hunter)
Product form	Nb/FeNb bar	Ta powder
Development	**Next generation capacitors**	Higher performance capacitor

Nb, a potential substitute of Ta for next generation capacitors

Hunter process

$$K_2TaF_7(l) + 5\ Na(l) \rightarrow Ta(s) + 5\ \mathbf{NaF}(l) + 2\ \mathbf{KF}(l)$$

Diluent

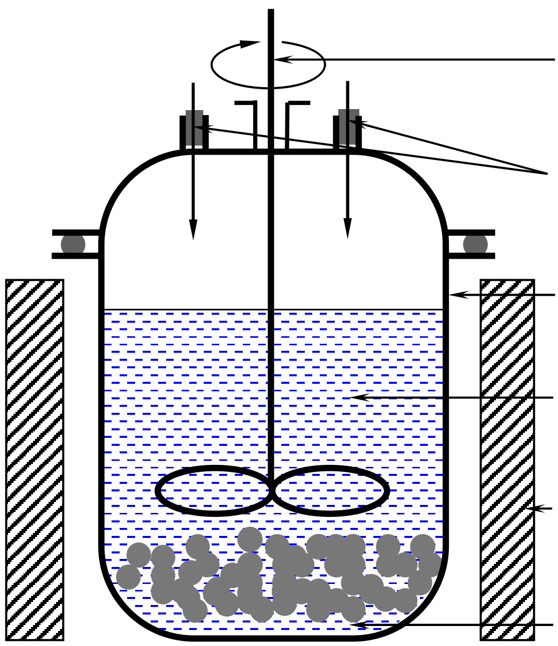


Figure Schematic illustration of the Hunter process.

Features

◎ Well controlled powder purity and morphology

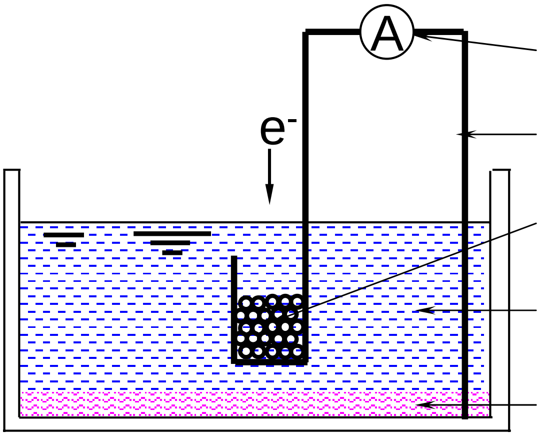
× **Batch** type process

× **Time and labor consuming** reduction process followed by mechanical and hydrometallurgical separation operations

× Large amount of **fluorides** wastes

Direct reduction processes of oxide

(a)

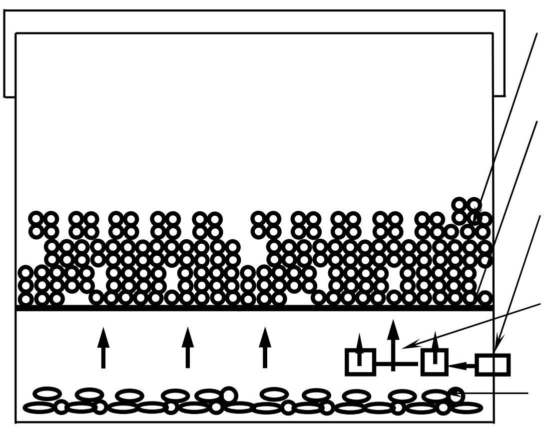


Okabe, *et al.* 1999

$Nb_2O_5 + 10 e^- \rightarrow 2 Nb + O^{2-}$

$5 Ca \rightarrow 5 Ca^{2+} + 10 e^-$

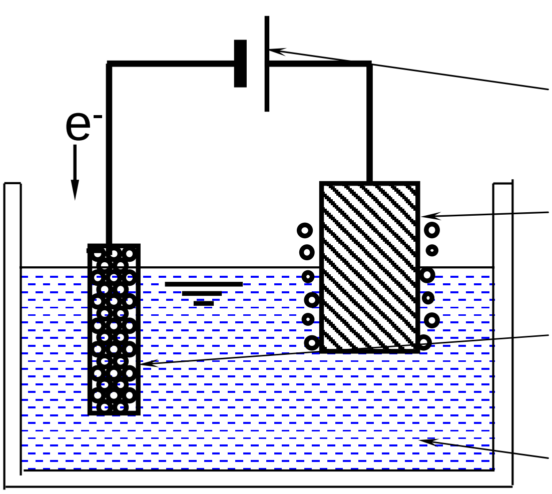
(b)



H.C.Starck, 2001

$Nb_2O_5 + 5 Mg \rightarrow 2 Nb + 5 MgO$

(c)

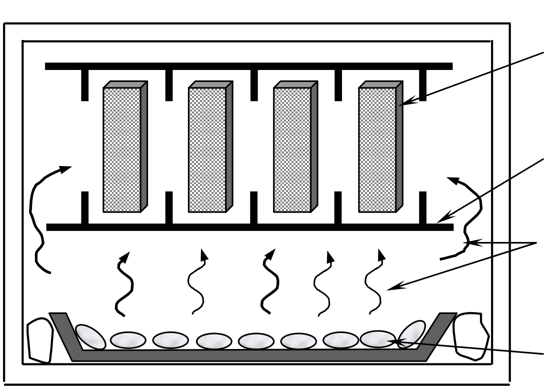


Fray, *et al.* 2002

$Nb_2O_5 + 10 e^- \rightarrow Nb + 5 O^{2-}$

$C + x O^{2-} \rightarrow CO_x + 2x e^-$

(d)



Okabe, *et al.* 2003

$Nb_2O_5 + 5 Mg \rightarrow 2 Nb + 5 MgO$

Objectives of this study

To develop a **new, low cost, high quality** niobium powder production process for capacitor or other electronic applications.

Essential process features:

◎ **fine and homogeneous** niobium powder have to be obtained.

◎ **purity and morphology of the niobium powder have to be controlled.**

○ the process is required to be **low cost** and efficient,

◎ (semi-) **continuous**,

○ environmentally sound.

Electrochemical Pulverization (EP)

Anodic:	Nb (bulk, *s*)	→	Nb^{n+} (*l*) + n e^-
Cathodic:	n Dy^{3+}(*l*) + n e^-	→	n Dy^{2+} (*l*)
Redox reaction in molten salt:	**Nb^{n+} (*l*) + n Dy^{2+}(*l*)**	**→**	**Nb (powder, *s*) + n Dy^{3+}(*l*)**

Overall Reaction : Nb (bulk, *s*) → Nb (powder, *s*)

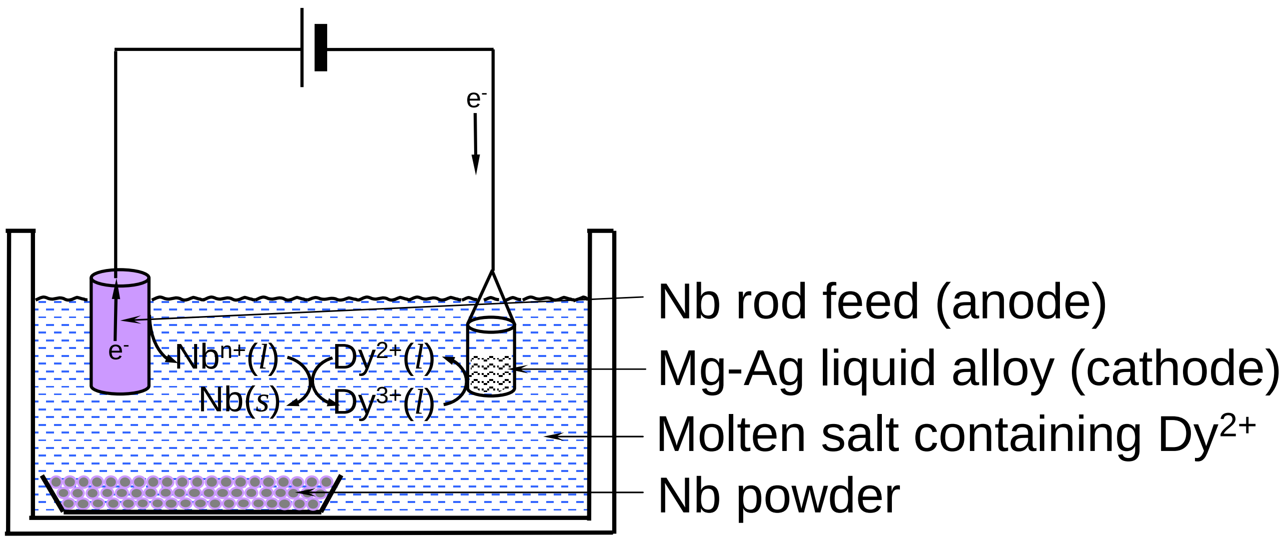


Figure Schematic illustration of the configuration of EP.

Features:

◎ **Fine** powder production by **homogeneous ionic redox reaction.**

◎ **Purity and morphology can be controlled by:**
dissolution speed of Nb bulk,
concentration of Dy^{2+} ions reductant,
temperature.

◎ **Low cost**:
cheap ATR Nb ingot feed can be used.

○ Environmentally sound:
reductant is not consumed,
molten salt can be reused.

Thermodynamic analysis

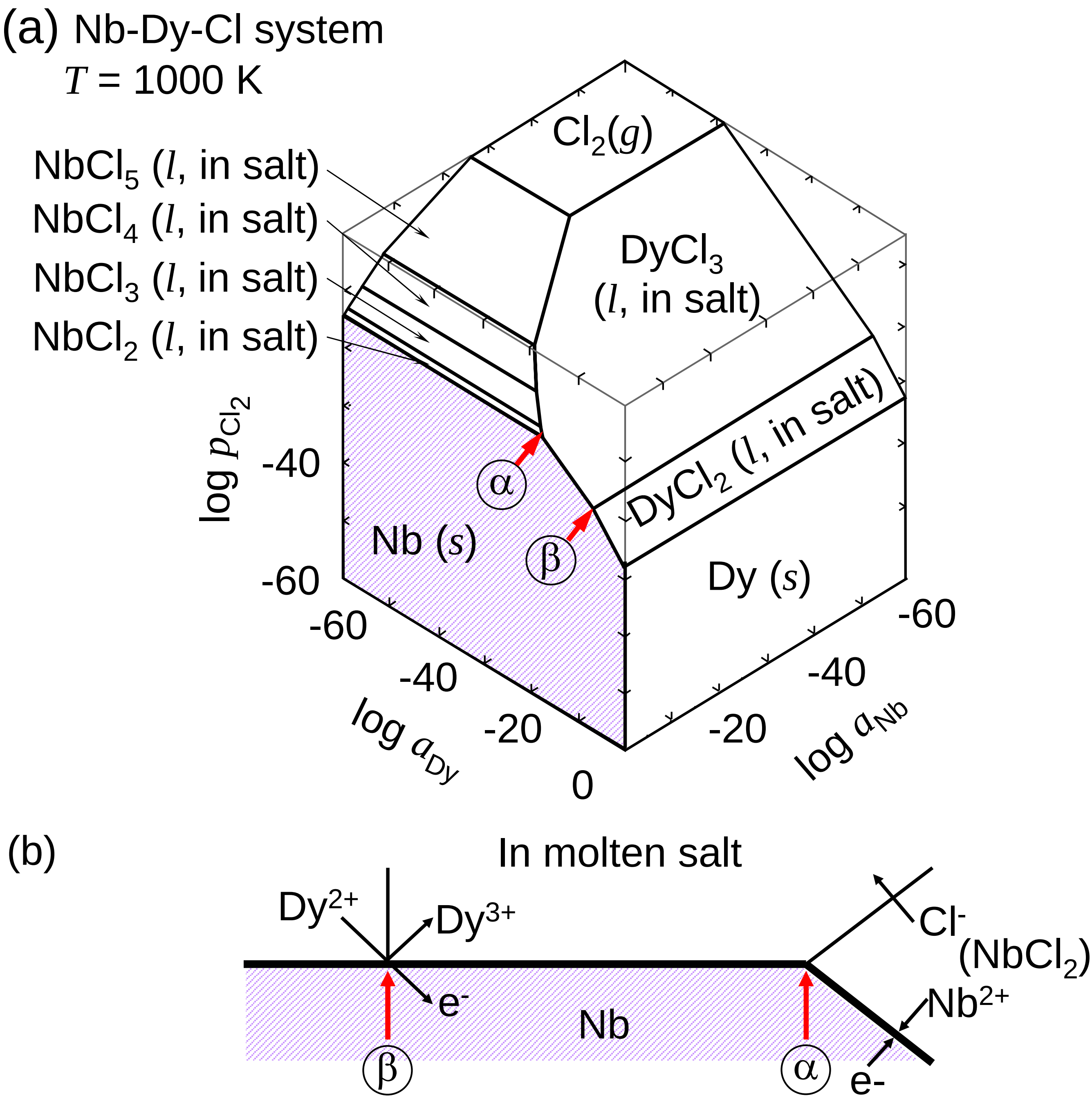
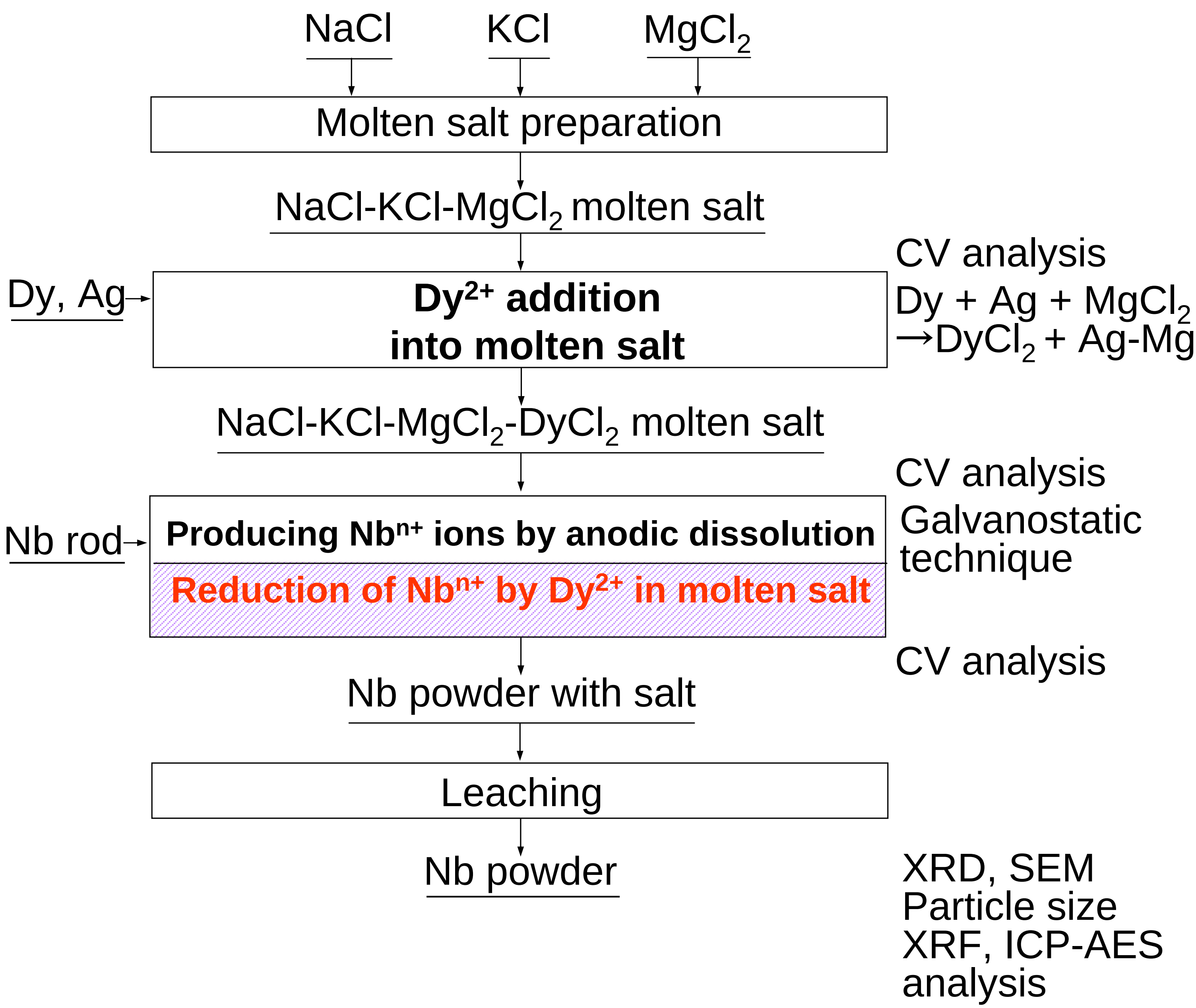


Figure (a) Three dimensional chemical potential diagram for the Nb-Dy-Cl system at 1000 K. (b) A mechanism for niobium powder production using Dy^{3+} /Dy^{2+} equilibrium in molten salt.

Nb ions reduction using Dy^{3+}/Dy^{2+} equilibrium is thermodynamically feasible

Experimental procedure

(a) Flowchart of Experimental procedure

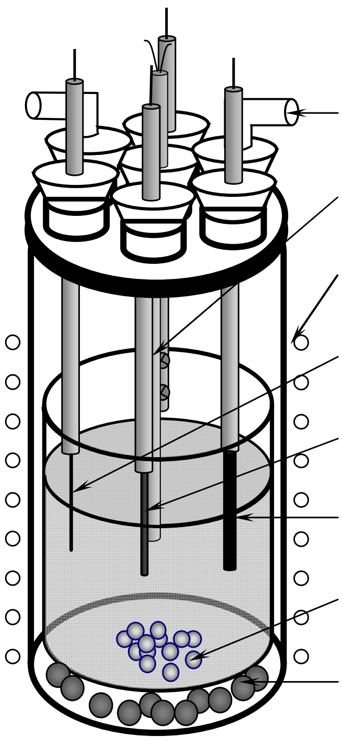


(b) Experimental conditions for EP of ATR-Nb

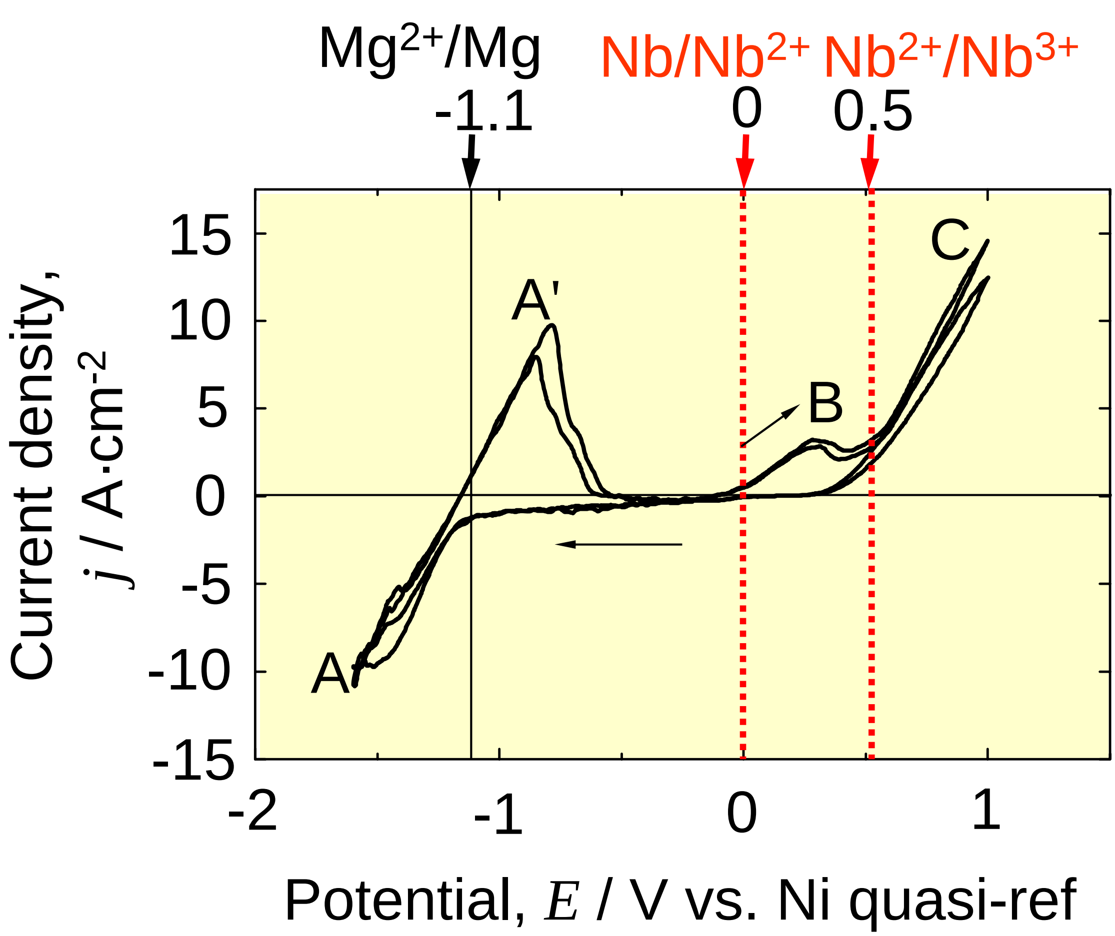
Exp. #	Dy add. w_{Dy} /g	Molten salt w_{ms}/g	Molten salt Composition (mol%)	Temp. T / K	Current i / A
A	30.5	1296	NaCl-36KCl-9MgCl$_2$-1DyCl$_2$	1000	2
B	50.1	1049	NaCl-36KCl-8MgCl$_2$-2DyCl$_2$	1000	2

Cyclic voltammogram of Nb

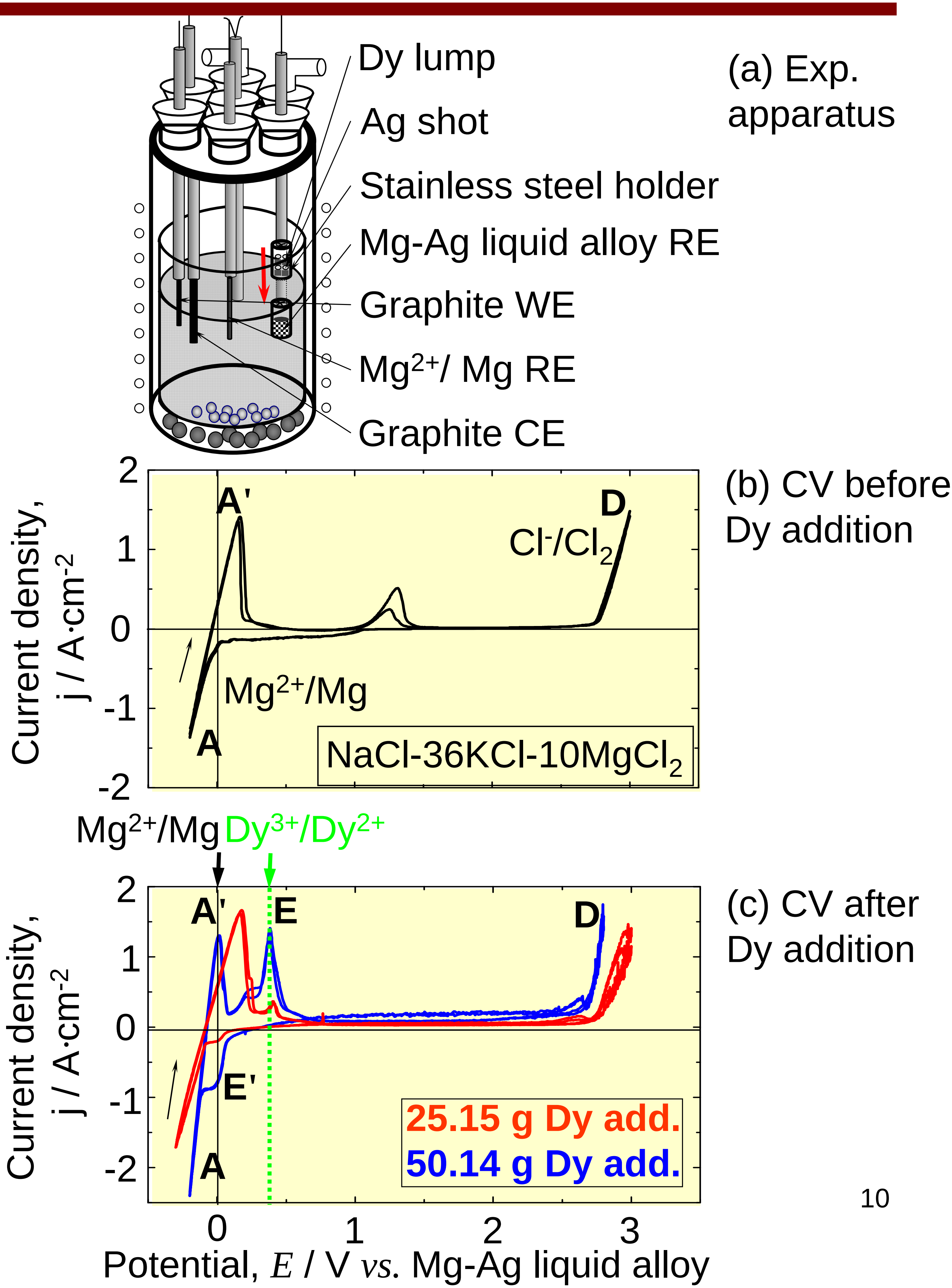
(a) Experimental setup



(a) Cyclic voltammogram of Nb in
NaCl-36 mol%KCl-10 mol%$MgCl_2$ molten salt

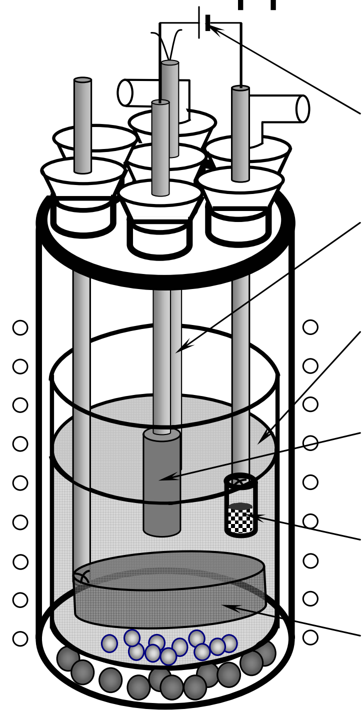


CV before and after Dy^{2+} addition

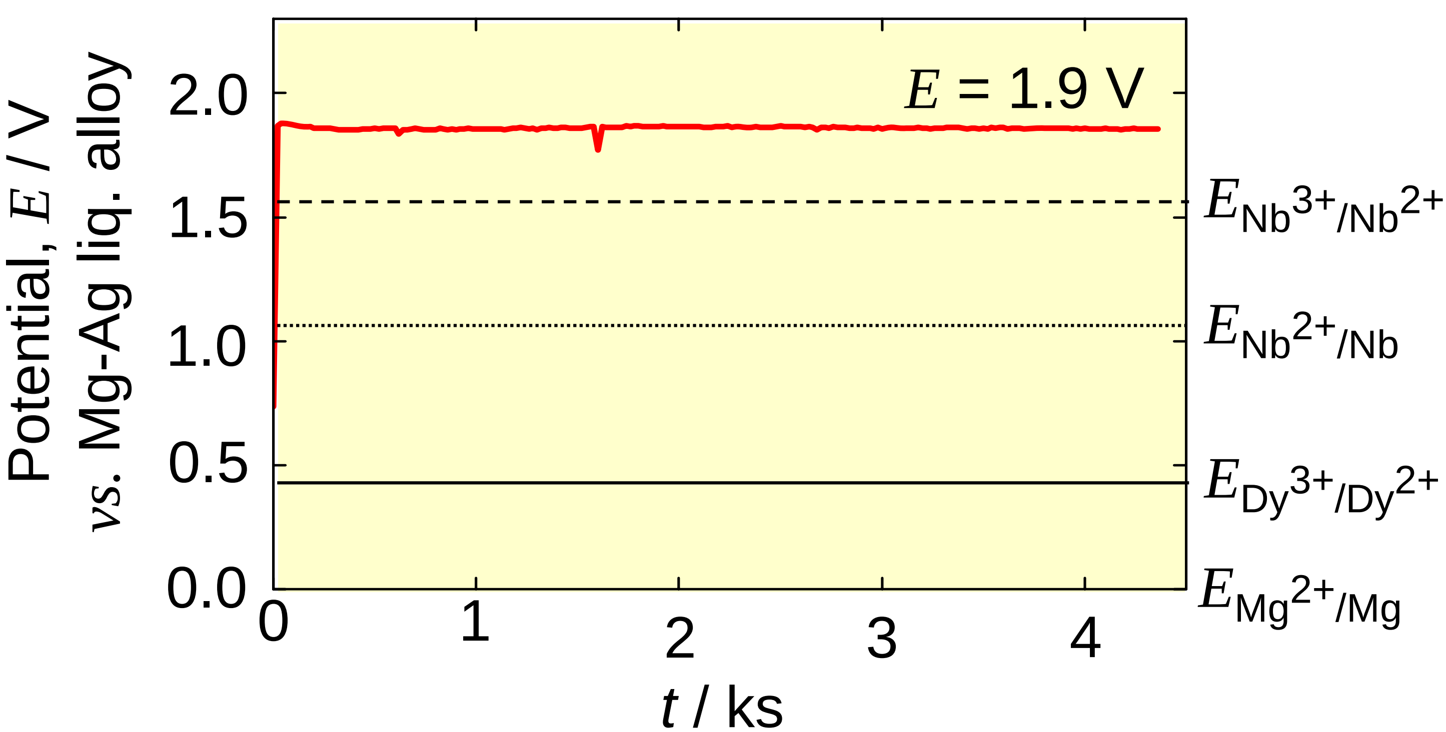


EP of Nb in Dy^{2+} containing molten salt

(a) Experimental apparatus for EP of Nb rod anode



(b) Chronopotentiomatric curve of Nb anode (i = 2 A)



Anodic current efficiency ($Nb \rightarrow Nb^{n+} + n\ e^-$)

n=2, 58%

n=3, 87%

Appearances before and after EP

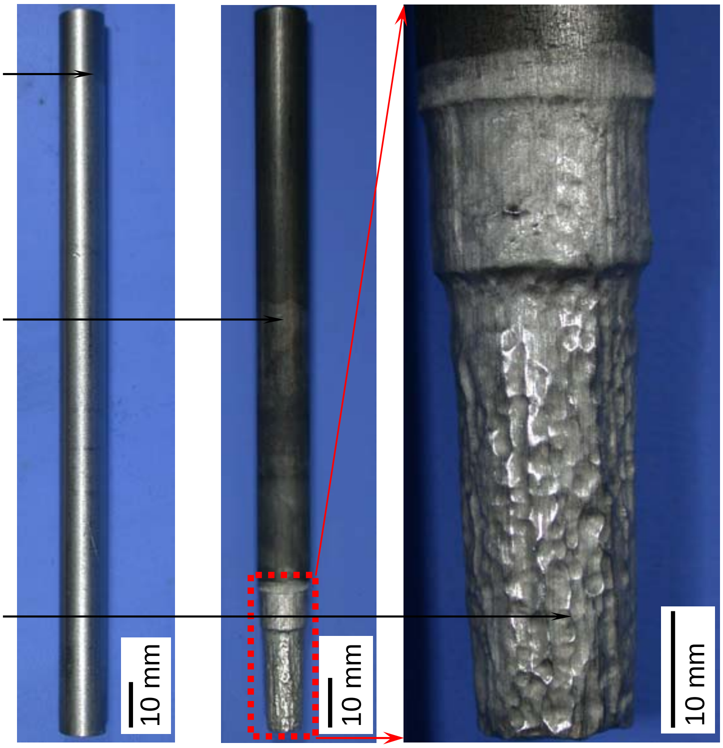
(a) Nb anode before and after EP

Before | After EP

Initial Nb rod

dissolved Nb rod

Immersed part of Nb rod



Nb rod was dissolved

(b) Stainless steel holder of liquid alloy cathode after EP

Cathode current lead

Supporting rod for cathode

Stainless steel holder

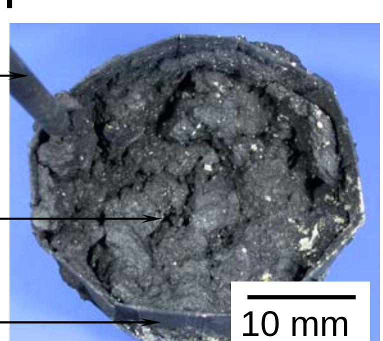
No Nb deposition on cathode was observed

(c) Nb deposits in powder collecting dish after EP

Supporting rod for collecting dish

Nb powder with salt

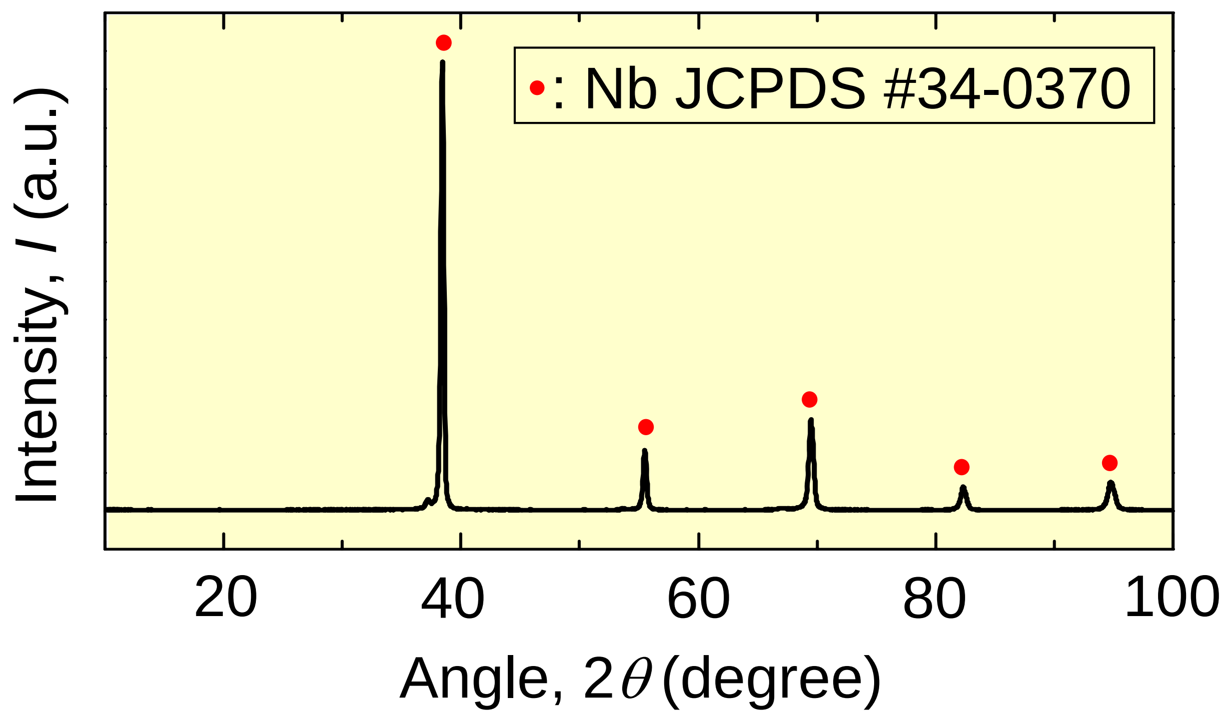
Collecting dish



Nb powder was obtained in collecting dish

XRD and XRF analysis

(a) XRD pattern of the Nb powder obtained by EP.



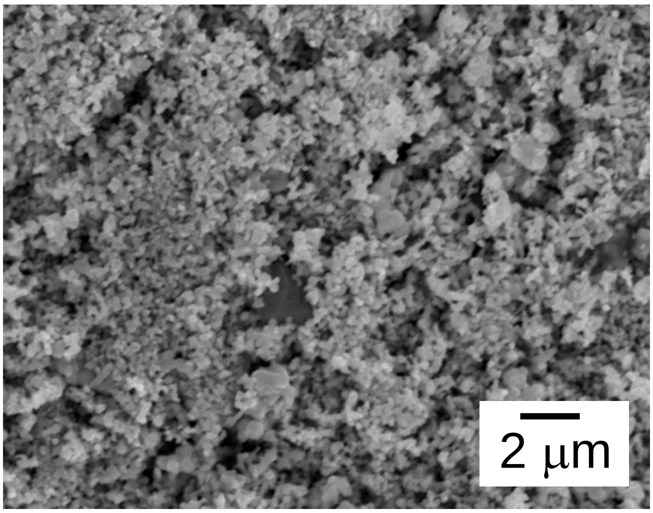
(b) XRF results of the Nb powder obtained by EP.

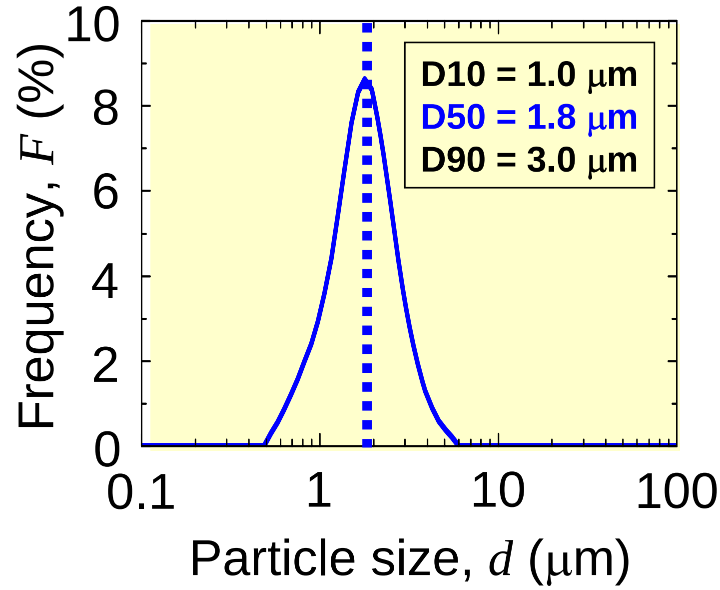
Exp. #	Concentration of element *i*, C_i (mass%)								Yield
	Nb	Fe	Cr	Ni	Ag	Mg	W	Ta	
A	**97.92**	0.12	0.01	0.14	<0.01	0.06	0.70	0.05	**92%**
B	92.68	2.93	0.90	0.23	<0.01	0.44	1.04	<0.01	**98%**

Presently, niobium powder with purity of 98 mass% was obtained.

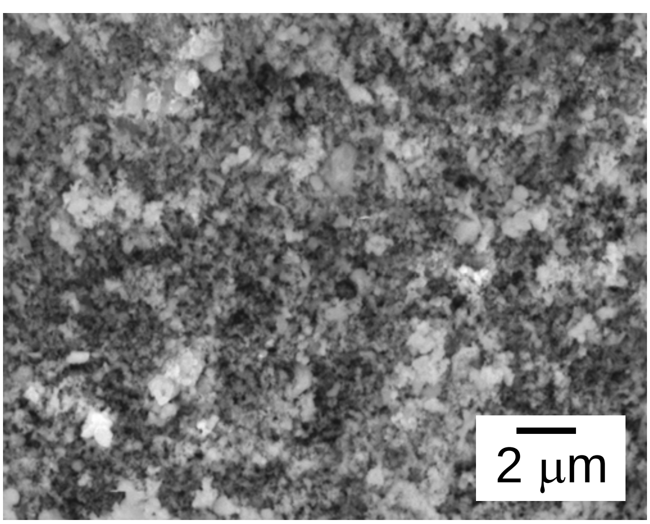
SEM and particle size analysis

(a) Exp. A: in NaCl-36 mol%KCl-9 mol% $MgCl_2$-1 mol% $DyCl_2$





(b) Exp. B: in NaCl-36 mol%KCl-8 mol% $MgCl_2$-2 mol% $DyCl_2$



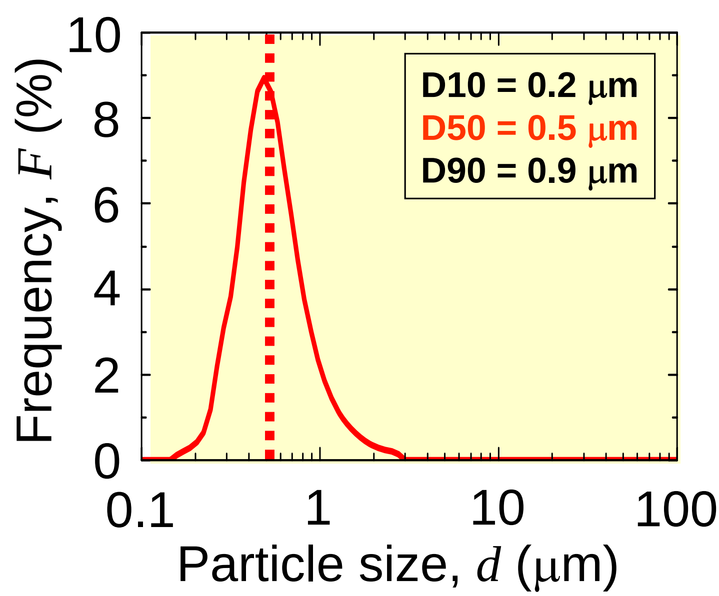


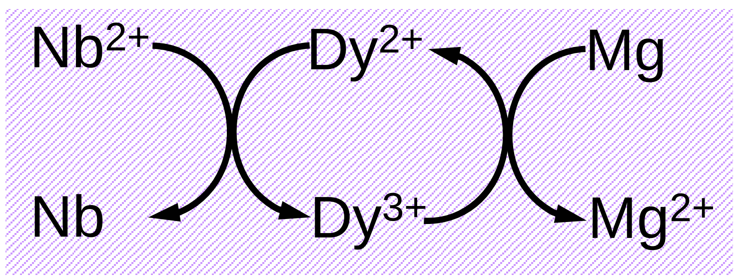
Figure SEM image and particle size distribution profile of the Nb powder obtained by EP technique.

Fine and homogeneous Nb powder was obtained

Summary and future work

Summary:

The electrochemical pulverization technique of bulk niobium in molten NaCl-KCl-$MgCl_2$ salt containing Dy^{2+} ions was demonstrated to be **effective in producing fine and homogeneous** niobium powder.



Future work:

- Development of **powder purity and morphology controlling** techniques.

- Improvement of **current efficiency.**

⬇

Development of the electrochemical pulverization technique to be applied to the production technology of niobium powder for **next generation high performance capacitors.**