Enrichment of ^{41}K isotope in potassium formed on and in a rhenium electrode during plasma electrolysis in K_2CO_3/H_2O and K_2CO_3/D_2O solutions

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Abstract

It was found that potassium forms on rhenium electrodes during plasma electrolysis in K_2CO_3/H_2O and K_2CO_3/D_2O solutions, and the new potassium has unnatural isotopic ratios. The isotope ^{41}K increases from the natural abundance, 6.7%, to as much as 32–37%. The percentage of ^{41}K in the potassium contamination in a rhenium electrode before electrolysis was close to the natural isotopic abundance (6.7%). This result suggests that the ^{41}K was enriched by some unknown process connected with a vigorous discharge of plasma electrolysis.

1. Introduction

In a previous study we observed strong glow emission from a tungsten electrode when electrolysing at a large current density above 3.5 A cm^{-2}. This is referred to as plasma electrolysis [1, 2]. The glow is different from a conventional electric arc in that it emits exclusively from the cathode. An analysis of the surface element composition of the tungsten electrode after the electrolysis could not be obtained because the cathode melted, dispersing material from surface layers and bulk as fine particles at the bottom of the electrolytic cell.

In the present study, it was found that a considerable amount of potassium was formed in the bulk and on the surface of a rhenium cathode after plasma electrolysis. The potassium atoms apparently constitute an intermetallic compound or alloy with rhenium atoms of the electrode material [3]. We investigated the isotopic distribution of potassium and found that significant enrichment of ^{41}K isotope takes place.

2. Experimental details

The electrolytic cell was made of fused quartz glass in the form of a flat-bottomed cylinder (6.2 cm dia. × 15 cm tall). The electrolytic cell is shown elsewhere [1, 2]. The working electrode was a cold-worked rhenium sheet (0.8–1.0 cm^2 nominal area, 0.1 mm thick). The counter electrode was a platinum mesh (1 cm × 7 cm, 80 mesh). The electrolytic cell was washed successively with acetone, Milli-Q water, hot mixed acid (1:1 H_2SO_4 + HNO_3) and Milli-Q water. The electrolyte solution was 0.5 M K_2CO_3 prepared from Merck sprapur reagent and Milli-Q water.

A regulated d.c. current/voltage power supply with maximum output potential of 160 V was used. Before plasma electrolysis was initiated, the cathode was conditioned with ordinary electrolysis for 1 h at a current density of about 2 A cm^{-2}, during which the temperature of the solution rose to 75–80 °C. Current density was then increased to 4 A cm^{-2} and several minutes later the electrode became incandescent with glow discharge, which we held for 7–19 min. The incandescent colour ranged from a blue-violet to reddish violet.

The element and isotope analysis of the electrode surface layers after the plasma electrolysis was carried out by Auger electron spectroscopy (AES) and time of flight secondary ion mass spectroscopy (TOF-SIMS). The AES measurement was made under 7×10^{-8} torr with an ANELVA AAS-200 Auger electron spectrometer, 3.0 keV beam energy, 2.5 A of filament current, and 0.3% resolution. The surface sputtering with Ar$^+$ ion bombardment was done under 2.5×10^{-5} torr of 99.9995% pure Ar gas. The TOF-SIMS measurement was made by the Ga$^+$ ion irradiation using a ULVAC-PHI. TFS-2100 TOF-SIMS spectrometer with 40 μm × 40 μm raster size and 0.01 a.m.u. resolution.

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3. Results and discussion

A typical example of the plasma electrolysis is shown in Figure 1. During the plasma electrolysis, sporadic bursts of the glow emission occurred, during which the colour of the glow turned from bluish violet to reddish violet. The former is caused by potassium plasma (wavelengths 404.72 and 404.41 nm) and the latter by potassium, deuterium (wavelengths 656.28, 486.13, 434.05 and 410.17 nm for hydrogen) and oxygen plasma (wavelengths 700.22, 645.61, 645.46, 445.37 and 436.83 nm) [4].

Figure 2 shows an example of AES spectra of an electrode after the plasma electrolysis in K_2CO_3/H_2O solution. A strong signal of potassium appears, showing that a significant amount of potassium was formed on and in the electrode during plasma electrolysis. The signal intensity decreases with increased sputtering time, indicating that most of the potassium is close to the surface. The approximate depth of the sputtered face was estimated as follows. First, the number of atoms, N,
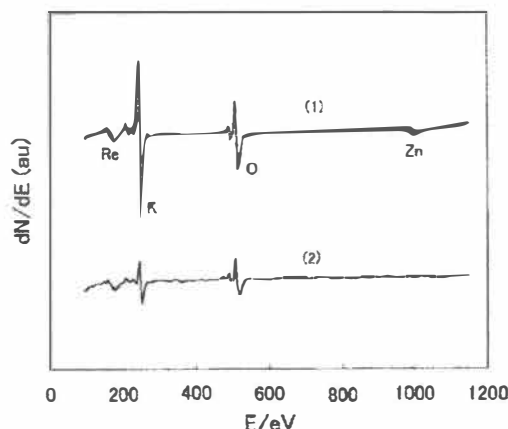
Fig. 2. Auger spectra of a rhenium electrode after plasma electrolysis in K_2CO_3/H_2O solution. Ar^- bombardment time: (1) zero, (2) 30 s.

removed from the electrode surface was estimated approximately by the following equation [5]:

$$N = f_{Re} N_{Ar^+} = \frac{f_{Re} J_{Ar^+} t}{1.6 \times 10^{-19}} \tag{1}$$

where N_{Ar^+} number of Ar^+ bombarded per unit area, J_{Ar^+} current density of the Ar^+ ion bombardment (~ 8.5 μA cm^{-2}), f_{Re} sputtering yield of rhenium (2.1 under the present conditions [6]), and t is sputtering time. The number of atomic layers removed was estimated from the ratio, $N/10^{15}$, on the assumption that the number of rhenium atoms per unit surface area is 1×10^{15}. Figure 3 shows the ratios of the atomic concentration of potassium to that of rhenium plotted against the depth of the electrode. Potassium atoms are distributed down to the depth of about 120 monolayers. The total amount of potassium is approximately 2×10^{16} atom. These potassium atoms are probably formed on the electrode surface in the form of an Re–K intermetallic compound or alloy [3]. Besides potassium, small amounts of zinc and iron were detected within a
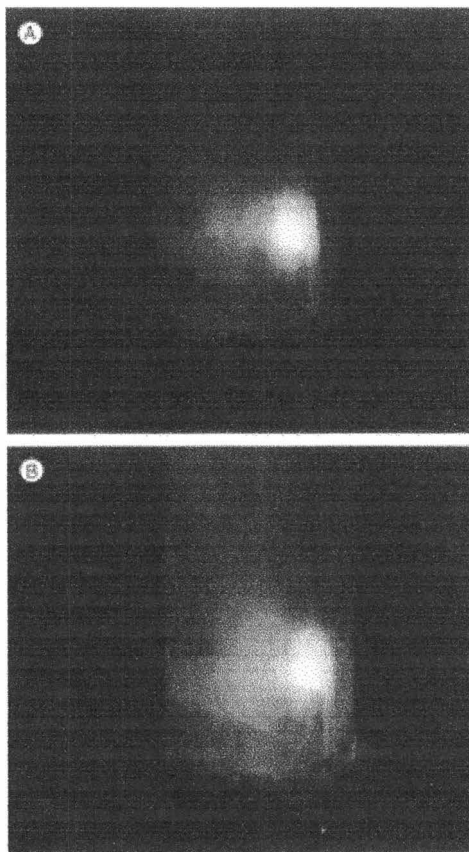
Fig. 1. Typical plasma electrolysis on a rhenium electrode in 0.5 M K_2CO_3/D_2O solution: (A) normal condition: the colour of the glow is bluish violet. (B) burst condition: the colour turns reddish violet. Similar behaviour was observed also in K_2CO_3/H_2O solutions.
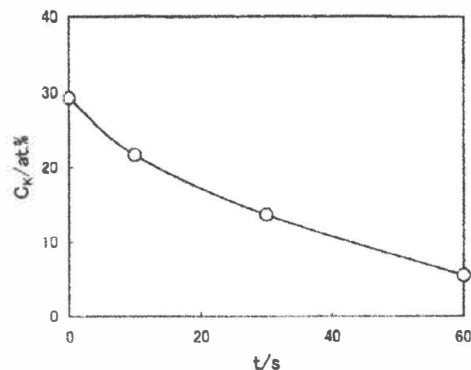
Fig. 3. Profile of the distribution of potassium atoms in a rhenium electrode (K_2CO_3/H_2O).

few monolayers. Similar results were obtained also in K_2CO_3/D_2O solutions.

After electrolysis, mass spectroscopy was performed for mass numbers ranging from 39 to 41, using TOFF-SIMS. The result is listed in Table 1, where the values of the signal intensities are of the particles present in the outermost layers and in the layers in the neighborhood of 20 monolayer, in samples electrolysed in ordinary water and heavy water. Among the ten major peaks detected, the strongest are those at mass numbers 38.9623, 39.9657, 40.0318, 40.9607 and 41.0422, corresponding to ^{39}K, ^{40}Ca, $^{12}C_3H_4$, ^{41}K and ^{40}CaH and $^{12}C_3H_5$, respectively. It is likely that two signals, ^{41}K and ^{40}CaH, are overlapping to generate one peak at 40.9607. However, the latter is negligible, because the signal intensity of ^{39}K is above 100 times stronger than ^{40}Ca and no Ca signal was detected on the AES spectra (Figure 2). The isotopic contents of ^{39}K and ^{41}K calculated from the signal intensities of 38.9623 and 40.9607 in Table 1 are shown in Table 2. As is evident from this Table, the isotopic contents of ^{41}K present in the outermost layers are 21.3 and 22.9 at %, having a tendency to increase towards the interior of the electrode. Thus, the contents of ^{41}K present in the neighborhood of 20 monolayer reach 31.9 and 36.8 at %. These values are far greater than the natural isotopic abundance of ^{41}K of 6.9 at %.

To confirm these results, it is essential to check on the accuracy of the TOFF-SIMS analysis. For this purpose, the measurement of the isotopic distribution of a small amount of potassium impurity in a fresh rhenium electrode was carried out, under the assumption that it must have natural isotopic abundance. The result is listed in Table 3. Before electrolysis, the cathodes have much less potassium than after electrolysis: usually the before: after ratio is 1:75. In a few spots on the cathode

Table 2. Isotopic distributions of ^{39}K and ^{41}K in the electrode calculated from signal intensities at mass numbers, 38.9623 and 40.9607, in Table 1

Electrode depth	Isotopic distributions* /%	
	^{39}K	^{41}K
(H_2O electrolysis)		
Outermost layers	77.1	22.9
Around 20 monolayer	63.2	36.8
(D_2O electrolysis)		
Outermost layers	78.7	21.3
Around 20 monolayer	68.1	31.9

*Natural isotopic abundance of ^{39}K and ^{41}K is 93.1 and 6.9, respectively.

surface it is 1:20. The isotopic ratios are easily computed from the ratio of signal intensity at 40.9664 to 38.9637. At first glance this ratio seems to indicate that the ^{41}K abundance in an unused cathode is far above the usual natural abundance. However, there is much more Ca contamination in the fresh electrode than K contamination, so the signal intensity of 39.9625 (^{40}Ca) is far larger than of 38.9637 (^{39}K), so the ^{40}CaH signal overlaps the ^{41}K signal, (whereas, as we noted above, in electrodes after electrolysis there is relatively much less Ca). The combined, overlapping signals of ^{40}CaH and ^{41}K come out as 40.9664. We estimated the amount of ^{41}K and subtracted that amount from the 40.9664 signal. We did this by assuming that the ^{39}K and ^{41}K in unused samples have normal isotopic ratios. After establishing much ^{39}K there is, we know that there is 7% of that mass of ^{41}K, which we subtract from the signal of 40.9664 signal, leaving only the ^{40}CaH signal. The result is shown in Table 4. The ratio of the signal intensity of ^{40}Ca to that of ^{40}CaH, I_{40Ca}/I_{40CaH}, is nearly

Table 1. SIMS signals of the particles with mass numbers ranging from 38.9623 to 42.9684 present on and in the electrodes after the plasma electrolysis

Mass	Count				Candidate species
	H_2O electrolysis		D_2O electrolysis		
	Outermost layers	About 20 monolayers	Outermost layers	About 20 monolayers	
38.9623 ± 0.0012	1919893	1995291	1886379	2036988	^{39}K
39.0223 ± 0.0011	914	—	1917	—	$^{12}C_3H_3$
39.0466 ± 0.0015	430	393	752	225	$^{39}SiH_9$
39.9657 ± 0.0023	18511	22166	15318	13456	^{40}Ca, ^{39}KH
40.0214	—	823	—	—	?
40.0318 ± 0.0025	13080	—	10942	122	$^{12}C_3H_4$
40.0582 ± 0.0030	—	678	—	349	$^{12}C_2^{11}BH_5$
40.0829	—	503	—	—	?
40.9607 ± 0.0006	569893	1161722	511535	954053	^{41}K, ^{40}CaH, $^{39}KH_2$, ^{39}KD
41.0422 ± 0.0045	99774	7939	88960	3372	$^{12}C_3H_5$
41.9671 ± 0.0191	415	309	400	194	^{41}KH, ^{42}Ca
41.9818	—	160	—	—	$^{40}CaH_2$
42.0041 ± 0.0057	1730	198	865	—	$^{12}C_2H_2O$
42.0437 ± 0.0021	20106	813	15432	220	$^{12}C_3H_6$
42.0696	—	157	—	—	$^{10}BH_6O$
42.9684 ± 0.0124	334	1566	204	473	^{43}Ca, ^{41}KD, $^{41}KH_2$

Table 3. SIMS signals of the particles with mass numbers ranging from 38.9637 to 41.0392 in a fresh electrode, in three different spots on the electrode

Mass	Count			Candidate species
	Spot 1	Spot 2	Spot 3	
38.9637 ± 0.0002	130115	26453	24351	^{39}K
39.0231 ± 0.0002	3603	1216	1631	$^{12}C_3H_3$
39.9625 ± 0.0005	264353	272925	93864	^{40}Ca
40.0300 ± 0.0010	568	301	266	$^{12}C_3H_4$
40.0477 ± 0.0005	–	1015	393	$^{12}C_2H_5{}^{11}B?$
40.9664 ± 0.0025	13920*	6792†	3558‡	$^{41}K, {}^{40}CaH$
41.0392 ± 0.0001	6450	2035	2682	$^{12}C_3H_5$

The mass values corresponding to *, $\dagger$, and $\ddagger$ marks are 40.9639, 40.9690 and 40.9657, respectively.

Table 4. Signal intensities of ^{41}K and ^{40}CaH of a flesh electrode calculated from signal intensities at mass numbers, 38.9637 and 40.9664, in Table 3, and the ratio of signal intensity of ^{40}Ca to ^{40}CaH

Spot	Count		I_{40Ca}/I_{40CaH}
	I_{41K}	I_{40CaH}	
Spot 1	8978	4942	53.5
Spot 2	1825	4967	54.9
Spot 3	1680	1878	50

the same at every part of the fresh electrode. This shows that the signal of 40.9664 is made up with the signals of ^{41}K and ^{40}CaH combined and the isotopic content of ^{41}K is very close to its natural isotopic abundance. This fact shows that the analysis of the isotopic distribution of potassium by TOF-SIMS is accurate and reliable.

4. Conclusions

The results leave no doubt that significant enrichment of ^{41}K in potassium formed on the rhenium electrode during plasma electrolysis takes place. With some elements, isotopes can be separated electrochemically by diffusing one isotope into the interior of the electrode, but this effect is very small and it must be repeated many times to achieve the apparent isotopic enrichment we observed. Furthermore, this technique does not work with potassium, because there is no chemical difference between ^{39}K and ^{41}K isotopes other than the difference in two neutrons. The fact that increased ^{41}K is found everywhere on the surface and in the interior of the electrode confirms this; if the isotopes were being separated, the missing ^{41}K would be found somewhere inside the electrode. Some unknown process connected with a vigorous discharge of the plasma electrolysis appears to cause the change in isotopic ratio. More careful investigations in various plasma electrolysis systems are needed to explain these results.

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