Studies on electrochemical dissolution of sintered molybdenum discs as a potential method for targets dissolution in $^{99\text{m}}\text{Tc}$ production

Izabela Cieszykowska¹ · Katarzyna Jerzyk¹ · Małgorzata Żółtowska¹ · Tomasz Janiak¹ · Grażyna Birnbaum¹

Received: 18 October 2021 / Accepted: 7 December 2021 / Published online: 20 December 2021
© The Author(s) 2021

Abstract

Electrochemical dissolution of pressed into discs and sintered metallic molybdenum powder with the mass of 712 ± 10 mg ($n = 15$) in potassium hydroxide solution was studied in detail. The technique was considered to apply for dissolution of irradiated ^{100}Mo target in the $^{99\text{m}}\text{Tc}$ production. The effect of various parameters, e.g., the concentration of the electrolyte solution, temperature, current density, and surface area of the platinum cathode, was investigated. The shortest time for total dissolution of molybdenum target was 70 min. This result was achieved using an electrolyte solution of 5 M KOH, temperature 55°C and the current density of 365 mA/cm^2 .

Keywords Electrochemical oxidation · Anodic dissolution · Cyclotron · Molybdenum · Technetium-99 m

Introduction

Technetium-99 m ($^{99\text{m}}\text{Tc}$) is widely used in nuclear medicine. It is often called the workhorse of modern medical imaging. Medical diagnostic imaging using $^{99\text{m}}\text{Tc}$ accounts for approximately 85% of all nuclear medicine procedures, representing around 30–40 million examinations worldwide every year [1]. Up to date, it is obtained in the decay of molybdenum-99 (^{99}Mo), isolated from uranium-235 (^{235}U) fission after its irradiation in a nuclear reactor [2, 3]. However, due to the aging of nuclear reactors involved in the production of ^{99}Mo , their extended maintenance periods, and, in certain cases, also shut down, the supply of ^{99}Mo might be uncertain [1, 4–6]. To prevent the shortages in $^{99\text{m}}\text{Tc}$ availability, alternative technologies for its production have been suggested [3, 7–28]. Out of these, there are two which seem to be most interesting: the direct production of $^{99\text{m}}\text{Tc}$ through the bombardment of ^{100}Mo with protons in a cyclotron in the nuclear reaction $^{100}\text{Mo}(p,2n)^{99\text{m}}\text{Tc}$ [11–20] and the photonuclear reaction with photon source from bremsstrahlung $^{100}\text{Mo}(\gamma,n)^{99}\text{Mo}$ [21–28]. In both methods, metallic molybdenum of high purity ($> 99\%$) enriched in ^{100}Mo as a target material is recommended [11, 15, 16, 29].

It's worth noting that targets made of pressed molybdenum oxide or molybdenum carbide were also used in the production of $^{99\text{m}}\text{Tc}$ [11, 18]. Nevertheless, metallic molybdenum is preferred due to its high melting point, resistance to high temperatures generated by the bombardment of charged particles, and high thermal conductivity. Molybdenum enriched in ^{100}Mo in the form of metallic powder is available commercially (99.815%, ISOFLEX, USA). However, the appropriate technique must be employed to prepare it in a durable target resistant to a high current beam. The approaches to prepare natural and enriched molybdenum targets included the use of foils [30], pressed and sintered powder [15, 16, 31], physical vapor deposition (PVD) [32], and electrophoretic deposition [33]. In our previous work, we demonstrated the manufacturing of a high-density ^{100}Mo metallic target using pressing of molybdenum powder into pellets and their subsequent sintering in a reductive atmosphere [31].

For the processing of ^{100}Mo , the irradiated target needs to be dissolved. Both the dissolution and the chemical separation of $^{99\text{m}}\text{Tc}$ from the irradiated target material should be fast because of the relatively short half-life of $^{99\text{m}}\text{Tc}$ (~ 6 h). Also, the chemical composition of solvent used for the target dissolution should be rather simple, preferably mono component, thus making further separation of $^{99\text{m}}\text{Tc}$ from the excess of molybdenum feasible. There are few approaches to the dissolution of metal molybdenum. The most common and well-defined is alkaline dissolution by the oxidation of metallic molybdenum to molybdenum trioxide or molybdic

✉ Izabela Cieszykowska
izabela.cieszykowska@polatom.pl

¹ National Centre for Nuclear Research, Radioisotope Centre POLATOM, Andrzej Sołtan 7, 05-400 Otwock, Poland

acid (VI) with 30% or 50% hot hydrogen peroxide and then dissolving the resulting precipitate in either NaOH, KOH, or $(\text{NH}_4)_2\text{CO}_3$ solutions [16, 34–40]. That process led to the formation of sodium/potassium/ammonium molybdate, according to the following reactions (1)–(4) given with NaOH as an example:

or

The time of molybdenum dissolution in 30% hydrogen peroxide depended on the physical form of Mo [34]. The 500–530 mg metal molybdenum foil and 720–760 mg metallic molybdenum powder pressed into disc dissolved within 3–5 min at 80 °C and within 2 min when the temperature was 90 °C. The pressed and sintered molybdenum disc with a mass of 720 mg dissolved under these conditions within 60 and 45 min, respectively. A significantly longer time of dissolution of sintered molybdenum results from less porous structure and hence increasing hardness and mechanical strength after a high-temperature process carried out in a hydrogen atmosphere [31]. There are reported results of a higher dissolution rate of molybdenum sintered discs [35]. However, hydrogen peroxide of a higher concentration of 50% was used in such a case. The average processing times of 600 g molybdenum discs depended on the brand of hydrogen peroxide used, ranging from 140 to 255 min.

The dissolution of molybdenum in inorganic acids was also reported [22, 41, 42]. However, molybdenum is insoluble in HCl, H_2SO_4 , HF, H_3PO_4 , and most other mineral acids, but it can be dissolved in HNO_3 [43]. The dissolution is fast in diluted HNO_3 and much slower in concentrated HNO_3 due to the formation of inert oxide film on the metal surface, making it difficult to dissolve. Guro et al. [41] studied in detail the hydrogen peroxide oxidation of molybdenum and its subsequent dissolution in concentrated nitric and sulfuric acids. They demonstrated that the dissolution of metallic molybdenum in hydrogen peroxide is based on the phenomenon of corrosion and corrosion inhibition, and the oxidation of molybdenum and associated reduction of the hydrogen peroxide is accompanied by heterogeneous catalytic hydrogen peroxide decomposition and oxygen release. Gumieła et al. [42] dissolved metallic molybdenum powder and irradiated with protons pressed and sintered natural molybdenum disc in 3.5 M HNO_3 . Azarov et al. [22] proposed dissolving gram amounts of metallic molybdenum subjected to irradiation in the linear accelerator in

a mixture of various inorganic acids resulting in obtaining soluble molybdenile salts. In such a way, they dissolved 30 g of molybdenum in the mixture of 53 ml, 56% nitric acid, and 51 ml, 40% hydrofluoric acid. Furthermore, researchers optimized the dissolution of 28.28 g of molybdenum in the mixture containing 54 ml of nitric acid and 123 ml of hydrochloric acid. The process lasted 2.5 h.

Regardless whether the acidic or alkaline dissolution is used, it should be adapted to the subsequent separation of $^{99\text{m}}\text{Tc}$ from the excess of molybdate. In order to selectively separate $^{99\text{m}}\text{Tc}$ from the dissolved target material using the solid phase extraction chromatography, we wanted to use the resin selective for $^{99\text{m}}\text{Tc}$ in the alkaline solution. In contrast to earlier published studies, in this work, we focused on the alkaline dissolution of pressed and sintered molybdenum target by electrochemical oxidation. The process was investigated and optimized towards complete and fast dissolution of molybdenum. To reach that goal, we explored whether external electromotive force (EMF) will shorten molybdenum dissolution time compared to chemical dissolution and if so, propose this method for dissolution of ^{100}Mo irradiated target. The dissolution by electrochemical oxidation was compared with the conventional dissolution method.

Several possibilities of electrochemical dissolution of molybdenum were reported [44–47]. However, described techniques are not adapted to our purpose. The vast majority of scientific papers refer to anodizing molybdenum to obtain a molybdenum oxide as a functional coating protecting against corrosion [46–54]. The literature on the electrochemical, quantitative dissolution of molybdenum is scarce and limited to non-aqueous media [48, 55]. In view of the above, the rapid, complete electrochemical dissolution of molybdenum is needed.

Molybdenum can be present in oxidation states from -2 to $+6$. However, its most common oxidation state in aqueous solutions at room temperature is $+6$ [56, 57]. The molybdate species in aqueous solutions depend on the molybdenum concentration and the pH. In neutral to mildly alkaline solutions, the monomeric MoO_4^{2-} predominates. As the pH decreases, the anion becomes protonated, and the following molybdate species are formed:

Molybdates tend to polymerize at higher molybdenum concentrations. At molybdenum concentrations above 10^{-3} mol Mo/L and pH 5–6, the heptamolybdate ion is formed, and at pH 3–5, octamolybdate predominates [56, 57].

Anodic dissolution of molybdenum depends mainly on the pH of the electrolyte [49]. The corrosion and passivation behavior of molybdenum in aqueous solutions at various pH was investigated using electrochemical impedance

spectroscopy and potentiodynamic polarization. These studies revealed that molybdenum metal surface was always covered with a passive film, which was more stable in acidic solutions [50]. The activation energy of dissolution of the molybdenum oxide film was lower in alkaline solutions (128.3 kJ/mol) than in neutral (152.5 kJ/mol) or acidic solutions (162.4 kJ/mol). This reflects the relative instability of the passive film in alkaline solutions, tending to metal dissolution.

The process of anodic dissolution of molybdenum in alkaline solution can be described by the following reactions (5)–(7) [46]:

Molybdenum oxides layer formed on its surface during molybdenum anodic dissolution is continuously dissolved in alkaline solution. The efficiency of the process depends on the concentration of the solution [46]. The electrochemical potential and pH of the solution affect the exact ratio between different valence states. Therefore, in our experiments, we investigated the influence of parameters such as the concentration of the electrolyte solution, the addition of 30% hydrogen peroxide, temperature, current density, molybdenum mass and surface area of the platinum cathode on the dissolution rate of pressed and sintered molybdenum discs.

Experimental

Materials and apparatus

Molybdenum foil (0.1 mm thick, 99.9% pure) used in preliminary experiments on electrochemical dissolution was purchased from Goodfellow Cambridge Ltd., UK. Natural metal molybdenum powder ($\geq 99.9\%$ chemical purity) with a particle size of 1–2 μm in diameter used to prepare pressed and sintered discs was obtained from Sigma-Aldrich, Poland. Molybdenum discs with a density of 9.4 g/cm³, a diameter of 12 mm, and a thickness of 0.6 mm were manufactured by pressing molybdenum powder, followed by their sintering in hydrogen flow at a temperature of 1600 °C [31]. The mass of each molybdenum disc was 712 ± 10 mg ($n = 15$) and corresponded to the mass of ¹⁰⁰Mo target irradiated in cyclotron [34]. Platinum foil (0.1 mm thick, 99.9% pure) serving as a counter electrode (CE) and platinum mesh (99.9% purity, nominal aperture: 0.12 mm, wire diameter: 0.04 mm, open

area: 56%) used as a counter electrode with a developed surface (CE) were obtained from Goodfellow Cambridge Ltd., UK. Lambda System (Poland) provided the Hg/HgO 6 M KOH reference electrode. Polyethylene foil doped with silica (Cookson Eutec, England) with pores diameter of $2 \div 4$ μm was used to separate cathodic and anodic chamber in an electrochemical cell. All used reagents were purchased with analytical grade from Sigma-Aldrich, Poland.

The Electrochemical Unit & Impedance Analyzer ATLAS 0531, Atlas-Sollich, Poland, interfaced with a PC was used for open-circuit voltage (OCV) measurements. Since the set ensured potential only up to 10 V, to optimize parameters for yielded dissolution of molybdenum, the Programmable DC Power Supply, type PPS3210, Motech Industries Inc., Taiwan, assuring voltage up to 30 V was applied. The IKA RW 20 digital mixer (Germany) was used to mix electrolyte solutions.

Electrochemical dissolution

The electrochemical dissolution of molybdenum was performed by the galvanostatic method. To determine the current–voltage parameters of the investigated electrochemical systems, open-circuit voltage (OCV) measurements were performed. For this purpose, three electrodes system was used with molybdenum as the working electrode (WE), platinum foil as the counter electrode (CE), and mercury/mercury oxide (Hg/HgO 6 M KOH) reference electrode (RE).

The electrochemical setup (Fig. 1) consisted of two electrodes: small pieces (1–5 cm²) of molybdenum foil or molybdenum disc with a surface area of about 3 cm² were

Fig. 1 Photograph of electrochemical setup used for molybdenum dissolution

used as the anode. The dissolving Mo disc was wrapped in Pt mesh, forming a pocket for the disc. Electrical contact was ensured through this mesh hanging on Pt wire. Platinum foil (3–21 cm²) or mesh served as a cathode. Before each electrochemical process, electrodes in the form of foils were cleaned with a surfactant, rinsed with distilled water, degreased with ethanol, re-rinsed in distilled water, and finally dried for 30 min at 100 °C. Due to the deposition of dissolved molybdenum on the opposite electrode, an electrochemical process was conducted in the vessel divided into two chambers by the separator made of polyethylene foil doped with silica. The catholyte and the anolyte solutions had the same composition and contained 1–5 M KOH. The selection of potassium hydroxide as electrolyte solution instead of more commonly used sodium hydroxide was justified by the greater solubility of molybdenum in the former one [58]. The volume of both catholyte and anolyte solutions was 13–20 ml. The anolyte solution was mixed during electrolysis with an overhead mixer at ~500 rpm. The process was carried out at constant current density in the range of 14–280 mA/cm² for molybdenum foil and of 80–755 mA/cm² for molybdenum sintered discs at ambient temperature and elevated to 55 °C. The effect of 30% hydrogen peroxide addition on the rate and the efficiency of electrochemical dissolution of molybdenum was investigated. To ensure the reliable effect of investigated parameters, all experiments were performed within 60 min. This time limit was associated with the time needed for the chemical dissolution of pressed and sintered molybdenum [34]. Since this method allowed molybdenum to be completely dissolved in less than 60 min, we assumed that our approach should provide no worse results. The efficiency of molybdenum dissolution was determined gravimetrically after drying the electrode.

Each experiment was repeated at least three times, and the presented curve and value describe the average result. Experiment errors were calculated using the commonly known standard deviation rule.

Results and discussion

Open circuit voltage (OCV) measurements

In order to assess the usefulness of the electrochemical cell for the dissolution of molybdenum, the voltage between two electrodes at an open-circuit voltage (OCV) was measured. The graph of voltage between molybdenum electrode (2 cm², WE) and platinum electrode (3 cm², CE) immersed in KOH solutions (15 ml) of different concentrations is shown in Fig. 2. The negative values of registered voltage result from the way of electrodes connection: molybdenum electrode has lower standard potential (−0.20 V) than platinum electrode (+1.2 V), but since it is subjected for dissolution,

Fig. 2 Open circuit voltage (OCV) curves recorded for an electrochemical system containing molybdenum anode (2 cm²) and platinum cathode (3 cm²) immersed in KOH solutions (15 ml) of various concentrations. The measurements performed at ambient temperature

it is connected as the working electrode. As depicted in Fig. 2, the voltage between these two electrodes increases with the increasing concentration of electrolyte solution. This is due to the increase of ionic conductivity in more concentrated KOH solutions. To verify a dominant oxidation state and type of chemical species formed by molybdenum in the investigated solution, molybdenum anode versus Hg/HgO 6 M KOH reference electrode potentials were measured. Recorded values were then recalculated to the potentials versus normal hydrogen electrode (NHE). The measurements were performed for the OCV system comprised of molybdenum foil (1 cm²) as a working electrode (WE) and Hg/HgO 6 M KOH counter electrode (CE). The electrolyte was divided into two solutions: catholyte and anolyte solutions containing 13 ml of 3 M KOH each. The measurements were conducted through a salt bridge saturated with 3 M KOH. The exact measurements were repeated for the platinum electrode (3 cm²). The obtained results indicate that the potential of molybdenum and platinum electrodes versus Hg/HgO 6 M KOH electrodes is accordingly −0.443 V and −0.045 V, which after recalculation for NHE gives −0.399 V and 0.089 V, respectively. According to the Pourbaix diagram [56], for calculated potential and pH of 14, the molybdenum half-cell exists in the area of MoO₄^{2−}, whereas platinum half-cell in the area of Pt_{cryst}.

Effect of current density

The preliminary experiments of the electrochemical dissolution of molybdenum were performed for molybdenum foil with a lower mass of 60 mg. The effect of current density on voltage was investigated. The results obtained for dissolution

of molybdenum anode (60 mg, 1 cm²) in 13 ml 3 M KOH are presented in Fig. 3. As was expected, the higher the current density, the greater the working electrochemical cell voltage.

Figure 4 illustrates the influence of current density on the dissolution of 60 mg metal molybdenum in 3 M KOH. The efficiency of molybdenum dissolution increases linearly with current density. It can be seen that at the current density of 15 mA/cm², only 15 ± 2% (*n* = 5) of molybdenum was dissolved. Increasing this parameter to 60 mA/cm² improved the yield to 56 ± 3% (*n* = 5), whereas almost all molybdenum, 99 ± 1% (*n* = 5), was dissolved when applying a current density of 100 mA/cm².

Effect of initial molybdenum mass

As expected, the rate and effectiveness of electrochemical dissolution were mass—dependent. When using the constant current of 100 mA and room temperature conditions, molybdenum anode with the mass of 60 mg (Mo foil with a thickness of 0.1 mm) entirely dissolved in 13 ml 3 M KOH after 60 min. Under the same conditions, the dissolving efficiency of pressed and sintered molybdenum disc with a mass of 712 ± 10 mg and thickness of 0.6 mm (*n* = 15) reached only 23 ± 1% (*n* = 3). It is worth mentioning that not only molybdenum mass but also thickness of molybdenum anode can significantly affect dissolution rate. Considering two molybdenum discs of the same mass but different thicknesses, the surface of the one with the smaller thickness will be greater. The larger the metal surface, the greater the contact area of the metal with the solution, and thus the faster dissolution. This applies not only to chemical dissolution but also to electrochemical dissolution.

Fig. 3 Current density versus voltage in electrochemical cell containing molybdenum anode (60 mg, 1 cm²) and platinum cathode (3 cm²). The measurements performed in 3 M KOH (13 ml) at ambient temperature

Fig. 4 Influence of current density on the efficiency of electrochemical dissolution of molybdenum foil (60 mg, 1 cm²) in 13 ml of 3 M KOH. The experiments were conducted versus platinum cathode (3 cm²) at ambient temperature

Effect of platinum cathode surface area

The attempts to improve the electrochemical dissolution of 712 ± 10 mg (*n* = 15) pressed and sintered molybdenum disc by increasing platinum cathode surface area gave no satisfying results (Fig. 5). After increasing the platinum cathode surface area from 3 to 21 cm², the yield of molybdenum dissolution remained at the same level of 23 ± 2% (*n* = 4). Simultaneously, it was observed that the increase of the platinum surface area from 3 cm² to 21 cm² reduced voltage between the electrodes from 9.4 ± 0.4 V (*n* = 4) to 5.2 ± 0.6 V (*n* = 4), respectively. Replacement of platinum foil with a platinum mesh of the same size, hence increasing the surface of the platinum electrode, resulted in a further decrease of voltage to 3.3 ± 0.4 V (*n* = 4). This is an essential observation since while the increase in current density increases voltage (Fig. 3), the reduction of

Fig. 5 Influence of platinum cathode surface area on the efficiency of electrochemical dissolution of molybdenum with the mass of 712 ± 10 mg (*n* = 15) in 3 M KOH. The experiments were performed at a current density of 100 mA/cm² at ambient temperature

the voltage with the extension of platinum cathode dimensions allows to use higher current densities, resulting in increased rate and efficiency of molybdenum dissolution (Fig. 4).

Effect of potassium hydroxide concentration

Figure 6 illustrates the effect of potassium hydroxide concentration of 1, 3, and 5 mol/dm³ on the electrochemical dissolution of molybdenum at room temperature and current density of 285 mA/cm². In 1 M KOH, molybdenum did not dissolve. The yield of dissolution increased with the concentration of KOH and reached $23 \pm 2\%$ ($n=4$) for 3 M KOH and $37 \pm 2\%$ ($n=4$) for 5 M KOH. However, particulates dark brown-colored of a near colloidal nature came off the anode.

Effect of hydrogen peroxide addition

It was found that the addition of 1 ml of 30% hydrogen peroxide per 20 ml of alkaline electrolyte solution increased the yield of molybdenum dissolution. This effect improves with the increase of KOH concentration. As shown in Fig. 7, the efficiency of molybdenum dissolution in electrolytes containing 1 M, 3 M, and 5 M KOH doped with 1 ml of 30% hydrogen peroxide achieved $22 \pm 3\%$ ($n=4$), $62 \pm 3\%$ ($n=4$) and $72 \pm 3\%$ ($n=4$), respectively. However, when the volume of 30% hydrogen peroxide was increased to 2 ml, the electrochemical dissolution yield decreased to $38 \pm 2\%$ ($n=4$). This effect is illustrated in Fig. 8.

Fig. 6 Influence of potassium hydroxide concentration on the efficiency of electrochemical dissolution of molybdenum. The measurements recorded for dissolution of 712 ± 10 mg ($n=15$) pressed and sintered molybdenum discs at a current density of 285 mA/cm² and ambient temperature. The volume of the electrolyte solution was 20 ml

Fig. 7 Effect of 30% hydrogen peroxide addition to KOH solutions of various concentrations on the efficiency of electrochemical dissolution of 712 ± 10 mg ($n=15$) pressed and sintered molybdenum discs. The experiments performed versus 21 cm² platinum cathode, at a current density of 480 mA/cm², at ambient temperature

Effect of temperature

At an elevated temperature of 55 °C, the molybdenum electrochemical dissolution yield in 5 M KOH increased from $37 \pm 2\%$ ($n=4$) to $80 \pm 3\%$ ($n=4$). Such results were obtained when attempting to dissolve 712 ± 10 mg ($n=15$) molybdenum sintered discs at the current density of 100 mA/cm². However, at temperatures higher than 55 °C, foaming of the electrolyte and leaps of the voltage between electrodes were observed.

Fig. 8 Influence of hydrogen peroxide concentration in electrolyte solution on the efficiency of electrochemical dissolution of 712 ± 10 mg ($n=15$) pressed and sintered molybdenum disc. The experiments performed versus 21 cm² platinum cathode, at a current density of 480 mA/cm², at ambient temperature

Table 1 Influence of current density on the time of complete dissolution of pressed and sintered molybdenum discs

Mass of Mo discs (mg)	Current density (mA/cm ²)	Time of complete dissolution (min)
716	285	95 ± 2
722	335	74 ± 3
714	365	69 ± 1
722	400	83 ± 2
722	435	85 ± 2

The values are given as mean ± SD, $n = 4$

Determination of complete dissolution rate

In summary, the electrochemical dissolution of molybdenum was most efficient in 5 M KOH. The yield of $80 \pm 3\%$ ($n = 4$) was achieved in 5 M KOH solution at an elevated temperature of 55 °C, whereas at ambient temperature, the highest yield of $72 \pm 3\%$ ($n = 4$) was reached for the mixture of 5 M KOH and 30% hydrogen peroxide. In order to reduce the time needed for the complete dissolution of molybdenum anode, the influence of current density on dissolution rate was studied. Results are given in Table 1. It can be seen that the rate of dissolution of pressed and sintered molybdenum disc raised with increasing current density from 283 to 367 mA/cm². Time required for complete dissolution in this range of current density decreased from 95 ± 2 min ($n = 4$) to 69 ± 1 min ($n = 4$). Further increase of current density led to a slower dissolution rate. The shortest time required for complete electrochemical dissolution of sintered molybdenum disc with a mass of 712 ± 10 mg ($n = 15$) was about 70 min. As a result, a yellowish, clear solution was obtained. This color is most likely from the presence of molybdic acid (hydrated forms of molybdenum trioxide and related species) forming monohydrates $\text{MoO}_3 \cdot \text{H}_2\text{O}$ and dihydrates $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$. For further dissolution, after the electrochemical process, 2 ml of 30% hydrogen peroxide were added, and the yellow color disappeared.

Conclusions

This work presents the results of the electrochemical dissolution of pressed and sintered molybdenum discs, typically serving as targets for cyclotron production of $^{99\text{m}}\text{Tc}$ [31]. The shortest time for total dissolution of molybdenum target 712 ± 10 mg ($n = 15$) in mass was 70 min. This result was obtained using an electrolyte solution of 5 M KOH, temperature 55 °C, and the current density of 365 mA/cm². For complete dissolution of molybdenum, resulting in the formation of a colorless solution, the addition of 30% hydrogen peroxide was needed. These results are comparable to the

chemical dissolution method. The lower temperature used in electrochemical dissolution (55 °C vs. 90 °C in the chemical dissolution method) is easier to control. In the chemical process, high concentrations of reagents are used (oxidation of molybdenum by 30% or even 50% hydrogen peroxide as the first step of dissolution), the reaction is turbulent, exothermic, and the oxygen is released. For these reasons, the process of chemical dissolution of molybdenum must be monitored, and reagents should be added in portions. From that point of view, the electrochemical dissolution of molybdenum allows remote control by adjusting the current–voltage conditions. The method can be easily adopted for hot-cell operation and for automation. Nevertheless, the final choice of the method used for the dissolution of the molybdenum target will depend on a particular user. This work may help in making a choice giving closer insight into the electrochemical process.

Acknowledgements This work was supported with the funds awarded by the Ministry of Science and Higher Education in Poland within the agreement No. 3969/IAEA/2018/0, IAEA Research Contract No. 22652, and CERAD project, financed under Smart Growth Operational Programme 2014–2020, Priority IV, Measure 4.2.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

1. The NEA (2018) The Supply of Medical Radioisotopes. Medical Isotope Demand and Capacity Projection for the 2018–2023 Period, OECD Nuclear Energy Agency, Paris, France
2. The IAEA (2015) Feasibility of Producing Molybdenum-99 on a Small Scale Using Fission of Low Enriched Uranium or Neutron Activation of Natural Molybdenum. Technical Reports Series 478, Austria, Vienna
3. The NEA (2010) The Supply of Medical Radioisotopes. Review of Potential Molybdenum-99/Technetium-99m Production Technologies. OECD, Paris, France
4. Tolleson J (2016) Reactor shutdown threatens world's medical isotope supply. Earth Clim. <https://doi.org/10.1038/nature.2016.20577>
5. Pillai MR, Knapp FF Jr (2011) Overcoming the $^{99\text{m}}\text{Tc}$ shortage: are options being overlooked? J Nuc Med 52(2):15N–16N, 28N
6. Ballinger R (2010) Mo-99 shortage in nuclear medicine: crisis or challenge? J Label Compd Radiopharm 53:167–168
7. Naik H, Suryanarayana SV, Jagadeesan KC, Thakare SV, Joshi PV, Nimje VT, Mittal KC, Goswami A, Venugopal V, Kailas S (2013)

- An alternative route for the preparation of the medical isotope ^{99}Mo from the $^{238}\text{U}(\gamma, f)$ and $^{100}\text{Mo}(\gamma, n)$ reactions. *J Radioanal Nucl Chem* 295:805–816
8. Van Do N, Khue PD, Thien Than K, Van Loat B, Rahman MS, Kim KS, Oh Y, Lee HS (2009) Thermal neutron cross-section and resonance integral of the $^{98}\text{Mo}(n, \gamma)^{99}\text{Mo}$ reaction. *Nucl Instrum Methods Phys Res B* 267:462–468
 9. Chattopadhyay S, Sujata SD, Das M, Goomer NC (2008) Recovery of ^{99m}Tc from $\text{Na}_2[^{99}\text{Mo}]\text{MoO}_4$ solution obtained from reactor-produced (n, γ) ^{99}Mo using a tiny Dowex-1 column in tandem with a small alumina column. *Appl Rad Isot* 66:1814–1817
 10. Tsuchiya K, Mutalib A, Chakrov P, Kaminaga M, Ishihara M, Kawamura H (2012) Status of ^{99}Mo - ^{99m}Tc Production Development by (n, γ) reaction. In: *Proceeding of the 4th International symposium in material Testing Reactors JAEA-Conf 2011-003*, pp 137–141
 11. The IAEA (2017) *Cyclotron Based Production of Technetium-99m*. IAEA, Vienna, ISBN 978-92-0-102916-4
 12. Stichelbaut F, Jongen Y (2011) Design of accelerator-based solutions to produce Mo-99 using lowly-enriched uranium. *Prog Nucl Sci Technol* 2:284–288
 13. Guérin B, Tremblay S, Rodrigue S, Rousseau JA, Dumulon-Perreault V, Lecomte R, van Lier JE, Zyuzin A, van Lier EJ (2010) Cyclotron production of ^{99m}Tc : an approach to the medical isotope crisis. *J Nucl Med* 51:13N
 14. Beaver JE, Hupf HB (1971) Production of Tc-99m on a medical cyclotron: a feasibility study. *J Nucl Med* 12:739–741
 15. Martini P, Boschi A, Cicoria G, Zagni F, Corazza A, Uccelli L, Pasquali M, Pupillo G, Marengo M, Loriggiola M, Skliarova H, Mou L, Cisternino S, Carturan S, Melendez-Alafort L, Uzunov NM, Bello M, Alvarez CR, Esposito J, Duatti A (2018) In-house cyclotron production of high-purity Tc-99m and Tc-99m radiopharmaceuticals. *Appl Rad Isot* 139:325–331
 16. Schaffer P, Bénard F, Bernstein A, Buckley K, Celler A, Cockburn N, Corsaut J, Dodd M, Economou C, Eriksson T, Frontera M, Hanemaayer V, Hook B, Klug J, Kovacs M, Prato FS, McDiarmid S, Ruth TJ, Shanks C, Valliant JF, Zeisler S, Zetterberg U, Zavodszky PA (2015) Direct Production of ^{99m}Tc via $^{100}\text{Mo}(p, 2n)$ on small Medical Cyclotrons. *Phys Procedia* 66:383–395
 17. Bénard F, Buckley KR, Ruth TJ, Zeisler SK, Klug J, Hanemaayer V, Vuckovic M, Hou X, Celler A, Appiah J, Valliant J, Kovacs MS, Schaffer P (2014) Implementation of multi-curie production of ^{99m}Tc by conventional medical cyclotrons. *J Nucl Med* 55:1017–1022
 18. Richards VN, Mebrahtu E, Lapi SE (2013) Cyclotron production of ^{99m}Tc using $^{100}\text{Mo}_2\text{C}$ targets. *Nucl Med Biol* 40:939–945
 19. Targholizadeh H, Raisali G, Jalilian AR, Rostampour N, Ensaf M, Dehghan MK (2010) Cyclotron production of technetium radionuclides using a natural metallic molybdenum thick target and consequent preparation of [Tc]-BRIDA as a radio-labelled kit sample. *Nukleonika* 55:113–118
 20. Stevenson NR (2011) Technetium-99m produced by proton irradiation of a fluid target system. Patent US 20110280357
 21. Starovoitova VN, Tchelidze L, Wells DP (2014) Production of medical radioisotopes with linear accelerators. *Appl Radiat Isot* 85:39–44
 22. Azarov AI, Bocharov VA, Dolzhek MA et al (2014) Production of technetium in molybdenum target on linac and modeling technetium distillation. *Voprosy Atomnoj Nauki i Tekhniki, Probl Atomic Sci Technol Ser Nucl Phys A* 63:59–62
 23. Zawistowski T, Wronka S (2021) Simulation of ^{99}Mo production from 30 MeV electron linear accelerator. *Acta Phys Pol A No 4:451–453*. <https://doi.org/10.12693/APhysPolA.139.451>
 24. Mang'era K, Ogbomo K, Zriba R, Fitzpatrick J, Brown J, Pellerin E, Barnard J, Saunders Ch, de Jong M (2015) Processing and evaluation of linear accelerator-produced $^{99}\text{Mo}/^{99m}\text{Tc}$ in Canada. *J Radioanal Nucl Chem* 305:79–85
 25. Mang'era K, Alina M, Barnard J, Omotayo A, Brown P, Martin J, Carlson P, Saunders C, Hayward P (2011) Production, separation and evaluation of Tc-99m and Mo-99 from accelerator transmutation of Mo-100. *J Nucl Med* 52(Suppl 1):1439
 26. Bennet RG, Terry WK, Christian JD, Kirkham RJ, Petti DW (1999) A system of ^{99m}Tc production based on distributed electron accelerators and thermal separation. *Nucl Technol* 126:102–121
 27. Bertsche K (2010) *Accelerator Production Options for Mo-99*. SLAC National Accelerator Laboratory (SLAC)
 28. Danon Y, Block R, Harvey J (2010) Production of Mo-99 using 30-MeV electrons and a Mo-100 target. *Trans Am Nucl Soc* 103:1081–1082
 29. Gagnon K, McQuarrie S, Wilson J (2012) Production of technetium from a molybdenum metal target. Patent WO 2012139220A1
 30. Stolarz A, Kowalska JA, Jasiński P, Janiak T, Samorajczyk J (2015) Molybdenum targets produced by mechanical reshaping. *J Radioanal Nucl Chem* 305:947–952
 31. Cieszykowska I, Janiak T, Barcikowski T, Mielcarski M, Mikołajczak R, Chojiński J, Barlak M, Kurpaska Ł (2017) Manufacturing and characterization of molybdenum pellets used as targets for ^{99m}Tc production in cyclotron. *Appl Rad Isot* 124:124–131
 32. Skliarova H, Cisternino S, Cicoria G, Marengo M, Palmieri V (2019) Innovative target for production of Technetium-99m by biomedical cyclotron. *Molecules* 24:25
 33. Hanemaayer V, Zeisler SK, Buckley KR, Kluga J, Kovacs M, Bernard F, Ruth TJ, Schaffer P (2012) Solid targets for ^{99m}Tc production on medical cyclotrons. In: *14th international workshop on targetry and target chemistry*, AIP Conf Proc 1509:120–124
 34. Pawlak DW, Wojdowska W, Parus LJ, Mikołajczak R (2016) Application of Ana Lig resin for ^{99m}Tc separation from ^{100}Mo target irradiated in cyclotron. *App Radiat Isot* 113:75–78
 35. Tkac P, Rotsch DA, Chemerisov SD, Byrnes JP, Bailey JL, Wiedmeyer SG (2021) Large-scale dissolution of sintered Mo disks. *J Radioanal Nucl Chem* 327:617–626
 36. Tkac P, Vandegrift GF, Harvey J (2012) Dissolution of Sintered Mo Disks. Argonne National Laboratory: Report ANL/CSE–13/19 11
 37. Tkac P, Vandegrift GF, Nunn S, Harvey J (2013) Processing of sintered Mo disks using hydrogen peroxide. Argonne National Laboratory Report ANL/CSE-13/44 12
 38. Tkac P, Vandegrift GF (2014) Dissolution of sintered Mo disks. Argonne National Laboratory Report ANL/CSE-14/26 13
 39. Tkac P, Rotsch DA, Stepinski D, Makarashvili V, Vandegrift GF, Harvey J (2016) Optimization of the processing of Mo disks. Argonne National Laboratory Report ANL/NE-15/46 14
 40. Tkac P, Rotsch DA, Chemerisov SD, Bailey JL, Krebs JF, Vandegrift GF (2016) Optimization of the dissolution of molybdenum disks: FY-16 results. Argonne National Laboratory Report ANL/NE-16/28
 41. Guro VP (2008) Molybdenum dissolution in mixtures of H_2O_2 and concentrated HNO_3 and H_2SO_4 in the presence of tungsten. *Inorg Mater* 44:239–243
 42. Gumiel M, Dudek J, Bilewicz A (2016) New precipitation method for isolation of ^{99m}Tc from irradiated ^{100}Mo target. *J Radioanal Nucl Chem* 310:1061–1067. <https://doi.org/10.1007/s10967-016-4967-2>
 43. Patnaik P (2003) *Handbook of inorganic chemicals*. The McGraw-Hill Companies, New York, ISBN 0-07-049439-8
 44. Abbas Q, Binder L (2011) The electrochemical dissolution of molybdenum in non-aqueous media. *Int J Refract Hard* 29:542–546

45. Csanyi LJ, Horvath I, Galbacs ZM (1989) Peroxide derivatives of molybdenum (VI) in neutral and alkaline media. *Transit Met Chem* 14:90–94
46. Hull MN (1972) On the anodic dissolution of molybdenum in acidic and alkaline electrolytes. *J Electroanal Chem Int Electrochem* 38:143–157
47. Petrova M, Bojinov M (2009) A mechanism of anodic dissolution of molybdenum in weakly acidic and neutral electrolytes. *J Univ Chem Technol Metall* 44:286–290
48. Abd El-Rahman HA, Gad-Allah AG, Abou-Romia MM (1987) Anodization of molybdenum II. Electrical breakdown. *J Appl Electrochem* 17:899–904
49. Badawy WA, Gad-Allah AG, Abd El-Rahman HA, Abouromia MM (1966) Kinetics of the passivation of molybdenum in acids and alkali solutions as inferred from impedance and potential measurements. *Surf Coat Technol* 27:187–196
50. Badawy WA, Al-Kharafi FM (1997) Electrochemical behavior of molybdenum in aqueous solutions. *Bull Electrochem* 13:392–398
51. Badawy WA, Al-Kharafi FM (1998) Corrosion and passivation behaviors of molybdenum in aqueous solutions of different pH. *Electrochim Acta* 44:693–702
52. Gad-Allah AG, Abd El-Rahman HA (1987) Anodization of molybdenum. I. Galvanostatic anodization. *J App Electrochem* 17:1065–1074
53. Wang K, Li YS, He P (1998) In situ identification of surface species on molybdenum in different media. *Electrochim Acta* 43:2459–2467
54. Wilkstrom LL, Nobe K (1969) The Electrochemical Behavior of Molybdenum. *J Electrochem Soc* 116:525–530
55. Kuznietz M, Cotler C (1988) Progressive dissolution of molybdenum foils in liquid uranium at 1160°C. *J Nucl Mater* 160(2–3):196–200
56. Ciszewski A, Baraniak M (2006) Chemical and electrochemical activity of the elements in the environment of water, Poznan University of Technology Publisher In Polish
57. Saji VS, Lee ChW (2012) Molybdenum, molybdenum oxides, and their electrochemistry. *Chem Sus Chem* 5:1146–1161
58. Tkac P, Vandergrift GF (2016) Recycle of enriched Mo targets for economic production of $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ medical isotope without use of enriched uranium. *J Radioanal Nucl Chem* 308:205–212

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.