Electrochemical conversion pathways and existing morphology of arsenic(III) in anode-cathode separated electrolytic cells

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ABSTRACT

To explore the electrochemical conversion of arsenic at different voltages and pH, an open separated electrolytic cell with a platinum anode and a graphite cathode was selected for this paper. The form and concentration of arsenic in the anodic cell and cathodic cell were detected. Experimental results proved that at 40.0 V, As(III) in an acid electrolyte in the cathodic cell was firstly mainly reduced to AsH₃ with trace As(0) as intermediate. As the electrolysis time arrived at 27 min, pH in the cathodic cell jumped suddenly from acidity to alkalinity, accompanied by the majority of the remaining As(III) converting to As(V) for an instant. As time went on, As(III) and As(V) remained almost unchanged at the ratio of 1:3, and the reduction of As(III) became extremely weak in the alkaline environment. When pH in the cathodic tank was adjusted to keep it acid, As(III) was eventually converted to AsH₃. Compared with high voltage, at a low voltage of 1.0 V the cathode failed to achieve the potential of As(III) reduction and As(III) was eventually oxidized to As(V) in the acid catholyte. Electrochemical oxidation of As(III) in the open cathodic cell was likely caused by in-situ generation of peroxide from electrochemical reduction of O₂. Theoretical support for electrochemical oxidation of As(III) on a carbon cathode in neutral and weak alkaline media is provided in this study.

Key words | arsenic, conversion pathways, existing form, graphite cathode, separated electrolytic cell

HIGHLIGHTS

- Conversion pathway of As(III) on a graphite cathode was found in a divided cathodic cell.
- As catholyte pH jumped from acidity to alkalinity at 40 V, most As(III) was sharply oxidized.
- At 40 V, As(III) reduction to AsH₃ rapidly decreased at the pH jump.
- Only AsH₃ evolution took place in the cathodic cell with pH<1.5 at 40 V.
- At 1 V, only As(III) oxidation occurred in the cathodic cell.
INTRODUCTION

Arsenic (As) contamination is widely recognized as a global health problem. The distribution of As(III) and As(V) in natural water depends on the redox conditions and pH of water, and As(III) is prevalent in anoxic groundwater. Compared with As(V), As(III) is reported to have low affinity to the surface of various minerals and be difficult to remove, because it mainly exists as nonionic H3AsO3 in natural water with pH <9. Nevertheless, As(V) can be easily adsorbed on solid surfaces and removed easily. Since As(III) is more toxic (Mandal & Suzuki 2002), more mobile and more difficult for removal than As(V) (Raychoudhury et al. 2015; Nikic et al. 2016; Hussein & Abu-Zahra 2017), electrochemical (Kunz et al. 2018) and electro-Fenton pro-oxidation of As(III) into As(V) and electrochemical reduction of As(III) into As(0) (Brusciotti & Duby 2008) are promising and convenient methods to pretreat As(III) from aqueous solution. Compared with surface water, remediation of polluted groundwater is extremely difficult and requires large financial resources. Electrochemical technology is very suitable for remediation of arsenic contaminated groundwater, owning to the advantages of in-situ remediation, no need to add chemicals to the groundwater, no pollution and high efficiency (Lacasa et al. 2012). So, it is important to investigate the existing form and transform mechanism of As(III) during electrochemical experiments.

Various researchers have investigated the electrochemical reaction of As(III) using different electrodes at negative potentials in acid and basic media through potentiostatic methods (Dewalens et al. 1975). In early studies, As(III) at negative potentials was found to be reduced to As(0) and/or AsH3, and the yields of As(0) and AsH3 at negative potentials were significantly determined by the negative potentials, pH and cathode materials (Bejan & Bunce 2003; Cao et al. 2012). Low pH benefited the deposition of As(0) and the evolution of arsine (Smirnov et al. 2007).

Recently, the partial oxidation of As(III) at negative bias potentials has been reported. Ten per cent of As(III) was observed to transform into As(V) on TiO2 electrode at negative bias potentials in an air saturated solution, and superoxide (O2−) which was generated from the reduction of O2 was speculated to be the only oxidant (Fei et al. 2011). Transformation of As(III) to As(V) was highly accelerated by the small quantities of H2O2 produced from O2 reduction under the alkaline conditions (pH 10.0–11.0) that were produced automatically around the cathodic electrode (mixed metal oxide electrode) (Qian et al. 2015). Reinforced As(III) oxidation was realized by the electro-generated H2O2 from O2 reduction on a cathode of MoS2 ultrathin modified carbon felt nanosheets in alkaline media (Xue et al. 2017). Carbon-based materials including graphite, carbon black, carbon fiber and so on are ideal and are the most frequently used cathode materials for on-site electro-generation of H2O2 from O2 reduction with much lower cost than the traditional chemical addition approach. In the heterogeneous electro-Fenton oxidation process for As(III), carbon-based materials are usually used as a cathode to produce H2O2 as the ingredient of Fenton reagents in acid solution (Wang et al. 2014; Si et al. 2017; Si et al. 2018). It was discovered that the yield of
H$_2$O$_2$ in weak alkaline electrolyte was far richer than that in acid media (Leng et al. 2006), and the degradation rate of organic pollutant on nano-graphite cathode in neutral and weak alkaline electrolyte under an electro-Fenton system with MnO$_2$ as catalyst was higher than that under an acidic condition (Dong et al. 2018). The electrochemical behavior of As(III) in the heterogeneous electro-Fenton process with iron-based catalysts has been extensively studied. However, the specific pH and Eh conditions and electrochemical conversion pathways of As(III) under separated oxidation and reduction environments with carbon materials as cathode at high or low voltage throughout the whole ascending pH are not well-understood.

Based on these reports and the previous research results in our laboratory (Cui et al. 2010; Qin et al. 2020), in order to further understand the conversion process of As(III) on carbon materials as cathode in electrochemical or heterogeneous electro-Fenton oxidation experiments in neutral and weak alkaline media, an anode-cathode divided electrolytic cell with a platinum anode and a graphite cathode was selected in this study to conduct the electrochemical conversion of As(III) at different voltages and pH in open environment, especially the transformation of As(III) in the cathodic compartment. The As(III) reduction and oxidation process on a graphite cathode was explored in the whole ascending pH from 1 to 13. This study produced results about the conversion process of As(III) on graphite cathode at high and low voltage in acidic, neutral and weak alkaline media. Theoretical references for further in-situ electrochemical or heterogeneous electro-Fenton oxidation of As(III) on carbon materials as cathode in groundwater with neutral and weak alkaline pH are provided in this study.

**METHOD**

**Chemicals**

Tetrabutylammonium hydroxide, dipotassium EDTA, methanol and HNO$_3$ were purchased from Thermo Fisher Scientific (USA), of commercially available chromatographic grade. Other reagents of analytical grade were obtained from Sinopharm Chemical Reagent Co. Ltd, China grade. All solutions and subsequent dilutions were prepared using deionized water from a scientific nanopure water purifier (Thermo Fisher, USA) with a resistivity of less than 0.055 μS/cm. 1,000 ml of As(III) standard solution (1,000 mg/L) was prepared by dissolving 1.3203 g of As$_2$O$_3$ in the minimum amount of 4.0 M NaOH, diluting to 1 L and then adjusting it to pH 3.0 with 1.0 M H$_2$SO$_4$. All the experiments were performed at room temperature (25 ± 1 °C).

**Construction of the separated electrolytic cell**

Two-electrode electrolytic systems are often used in laboratory and field experiments on electrochemical treatment of pollutants (Si et al. 2017; Dong et al. 2018). In order to clarify the transformation of arsenic in practical application, a anode-cathode separated electrolytic system with two electrodes in open environment was selected. Both the anodic tank and cathodic tank were 5 cm in diameter, 7 cm in height and made from polymethyl methacrylate (PMMA). The anodic tank was separated from the cathodic tank, and a salt bridge was used to connect the anolyte and the catholyte (Figure 1(a)). Only two electrodes, namely an anode and a cathode, were used in the electrolysis of As(III), a platinum disk electrode (3 mm in diameter) with geometric area of 0.071 cm$^2$ which served as anode was placed in the anodic cell, and a graphite rod with diameter of 0.6 cm and height of 2.0 cm which served as cathode was placed in the cathodic cell. The divided electrolytic tank was put in a constant temperature water bath, and the temperature was maintained at 25 °C.

**Operation of the separated electrolytic cell**

30 mL of 0.1 M nitric acid solution containing 40 mg/L As(III) was added to the anodic cell and the cathodic cell respectively. 40.0 V voltage provided by a GPC-6030D constant-voltage DC source (GWinstek, China) was imposed to electrolyze As(III). The electrolysis experiments were conducted for 3, 6, 9, 12, 15, 18, 21, 24, 27, 30, 35, 40, 45, 50, 55 and 60 minutes.

To determine As(III) and As(V) in the anolyte and the catholyte during the electrochemical process, 0.4 mL water samples were withdrawn by a 1-mL pipette at certain
intervals, diluted and filtered through a 0.22-μm PTFE filter, then a high performance liquid chromatography-inductively coupled plasma mass spectrometer (HPLC-ICP-MS) was used to separate arsenic species and determine the concentration of As(III) and As(V) in the water samples with different reaction time.

To determine As(0) produced in the cathodic cell, four identical graphite rod electrodes were prepared and four sets of experiments were conducted for different times, specifically, the first experiment for 15 minutes, second for 30 minutes, third for 45 minutes, and fourth for 60 minutes. Then electrodeposited As(0) on the four graphite rod electrodes was dissolved into HNO₃ solution, and the contents of arsenic in the solution were analyzed by ICP-MS.

The new silver salt spectrophotometry was used to detect arsine produced in the cathodic cell, and the arsine was guided into a scrubber containing 2% AgNO₃ solution for the first 15 minutes through an exit glass tube which was connected to the cathodic tank by inleting air in drops, and then the scrubber was replaced by another successively at 15, 30 and 45 min. The concentration of the arsine in the AgNO₃ solution was determined by a 721 spectrophotometer (Shitianpu, China).

To measure pH of the anolyte and the catholyte during the electrochemical process, the electrode of a pH meter (Mettler Toledo, Switzerland) was inserted into the anolyte or the catholyte, and the pH values were read out at certain intervals.

To measure Eh of the anolyte and the catholyte at different reaction time, the electrode of an ORP (oxidation-reduction potential) meter (Dapu, China) was inserted into the anolyte or the catholyte, the Eh data read out (namely the Eh at power-on) as the electrolysis was carried out for 3, 6, 9, 12, 15, 18, 21, 24, 27, 30, 35, 40, 45, 50, 55 and 60 minutes respectively, then the power supply was immediately turned off and the Eh data read out at power-off, then the power was turned back on and continued electrolysing As(III).

**Analytical methods and calculations**

A CS300 electrochemical workstation (Koster, China) with a standard three-electrode system was used to detect As(0) produced in the cathodic cell. One graphite rod electrode before and after use as cathode for the electrochemical conversion of As(III) served as a working electrode, the other graphite rod was used as a counter electrode, and a saturated calomel electrode (SCE) worked as the reference one (Figure 1(b)).

The separation of arsenic species and the detection of arsenic concentration was conducted by HPLC-ICP-MS. Arsenic species were separated by a Series 200 HPLC.
(PerkinElmer, USA) with an automatic sample injector and directly introduced into ICP-MS. A C8 chromatographic column (PerkinElmer, USA) was used with the mobile phase containing 1 mM tetrabutylammonium hydroxide, 0.05 mM dipotassium EDTA and 0.05% methanol (pH 6.8). To detect concentration of arsenic, an ELAN DRC II ICP-MS (PerkinElmer, USA) equipped with an atomizer and a spray chamber was used. The ICP-MS normal operating parameters were as follows: RF power 1,100 W, lens voltage 7.25 V, nebulizer gas flow rate 0.98 L/min, auxiliary gas flow rate 1.2 L/min, and plasma gas flow rate 15.00 L/min.

The calculation formula of current efficiency is

\[\eta = \frac{m'}{m} \times 100\% = \frac{m'}{I \times t \times k} \times 100\% = \frac{(C_t - C_0) \times V}{(\sum_{i=0}^{n} I_i \Delta t) \times k} \times 100\% ,\]

\[k(g/(A \cdot h)) = \frac{M}{3600 \times n}\]

where \(\eta\) is current efficiency, \(m'\) is the actual product quality (g), \(m\) is mass of product (g) obtained according to Faraday’s law, \(I\) is current intensity (A), \(t\) is power-on time (h), \(k\) is the electrochemical equivalent (g/(A \cdot h)), \(F\) is Faraday constant (96,485 C/mol), \(M\) is molar mass of arsenic element (74.9216 g/mol), \(n\) is the gains and losses of electron.

**RESULTS AND DISCUSSION**

**The transformation of As(III) at high constant voltage**

**As(III) transformation in anodic cell**

The concentration of As(III) and As(V) in the anodic tank with different electrolytic time was determined, as shown in Figure 2(a). Before 24 min, As(III) concentration decreased rapidly, while As(V) increased. At 24 min, the transformation from As(III) to As(V) was stopped and only As(V) remained in solution. The conversion process of As(III) was proved to match a zero-order reaction kinetics equation:

\[C_t = -1.558t + 42.23 \quad (R^2 = 0.979) \quad (1)\]

where, \(C_t\) (mg/L) was the concentration of As(III), \(t\) (min) was electrolysis time.

With the electrolytic time increasing, pH in the anodic cell was decreased (Figure 2(b)) (Lacasa et al. 2012). During this pH range, As(III) existed as H$_3$AsO$_3$, and As(V) existed as H$_2$AsO$_4$. It was found, before 12 min, the oxidation-reduction potential (Eh) of the electrolyte in the anodic cell acquired from the measurement of ORP meter was about 500 mV and pH of the anolyte descended from 1.15 to 1.12; based on the Nernst equation at 25°C

![Figure 2](image-url)
\[ E_h = 0.559 + 0.0295 \log \frac{[H_3AsO_4]}{HAsO_2} - 0.059pH \] (Schüring et al. 2000) As(III) could be converted to As(V) under this condition. After 12 min, the Eh measured increased slowly and As(III) continued being oxidized. With the electrolytic time between 21 and 24 min, As(III) was completely converted to As(V), and simultaneously the Eh suddenly increased to 1,100 mV; according to the Nernst equation, the value of \( \log \frac{[H_3AsO_4]}{HAsO_2} \) became very large, so the Eh of the electrolyte suddenly rose. After 24 min, the Eh rose very slowly (Figure 2(b)). The conversion from As(III) to As(V) in the anodic cell was likely electro-catalyzed by platinum hydroxide formed on the electrode surface (Equations (3)–(6)) (Dai & Compton 2006; Rivas et al. 2009).

\[
\begin{align*}
2H_2O & \rightarrow 4e^- + O_2 \uparrow + 4H^+ \\
Pt + H_2O & \rightarrow Pt(OH) + H^+ + e^- \\
Pt(OH) + As(OH)_3 & \rightarrow Pt(OH)As(OH)_3 \\
Pt(OH)As(OH)_3 & \rightarrow PtOAs(OH)_3 + H^+ + e^- \\
PtOAs(OH)_3 & \rightarrow Pt + OAs(OH)_3
\end{align*}
\]

The current with different electrolytic time at 40.0 V is shown in Figure 3(a). As 40.0 V voltage was applied to electrochemical transformation of As(III), the current value which was shown on display screen of the constant voltage DC source was 110 mA at the beginning, and then the current increased with electrolysis time. As the electrolysis time reached 60 min, the current increased to 210 mA. In the process of constant voltage electrolysis, pH in the anodic cell decreased even lower, and pH in the cathodic cell increased to strong alkalinity, which improved the conductivity of the electrolyte and caused the current to increase. The relationship between the transformation percentage of As(III) into As(V) and the current efficiency in the anodic cell is shown in Figure 3(b). As the electrolysis time was between 12 to 15 min, the current efficiency reached the maximum of 2.3%.

**As(III) transformation in cathodic cell**

The concentration of As(III) and As(V) in the cathodic cell with 40.0 V voltage at different electrolytic time is shown in Figure 4(a) and 4(b). Before 27 min, As(III) concentration was slowly decreased from 40.453 mg/L to 29.823 mg/L, mainly converted into AsH3 with trace As(0) (Figure 4(a)). And this reduction process was in accord with the zero-order kinetics equation:

\[
C_t = -0.405t + 41.341 
\]

where \( C_t \) (mg/L) was the concentration of As(III), \( t \) (min) was electrolysis time.

After 27 min, As(V) was presented in the cathodic cell suddenly, and As(III) decreased rapidly from 19.968 mg/L at 28 minutes to 8.259 mg/L at 30 minutes. After 50 min,
As(III) was no longer transformed to As(V), As(III) and As(V) existed dynamically at a 1:3 ratio, and total concentration of As(III) and As(V) in solution remained almost unchanged; however, the reduction of As(III) was weakened extremely.

Meanwhile, in the cathodic cell pH jumped from acidity to alkalinity between 27 minutes and 30 minutes (Figure 4(c)), accompanied with the Eh of catholyte at the cathodic cell at 40.0 V (at power-on) which dropped quickly (Figure 4(c)). Because the distribution of arsenic species depended on pH and Eh, E(As(III)/As(V)) decreased with the increase of pH (Smedley & Kinniburgh 2002), which was clearly represented by the pourbaix (Eh–pH) diagram of arsenic species. At 28 min, pH in cathodic cell was 9.71, As(V)/As(III) was detected as 0.490, according to Nernst equation, the corresponding Eh0 calculated should be −23 mV, which was lower than 83 mV of the Eh measured at power-on. It was speculated that new active species with strong oxidation capacity might be generated in the cathodic cell, which induced the oxidation of As(III) to As(V). The Eh-pH track of catholyte on graphite cathode at 40.0 V (at power-on) and at power interruption with different electrolytic time is shown in Figure 4(d). Surprisingly, it was found that the Eh of the catholyte at pH jump from 5 to 12 was higher than the stable fields of As(III)/As(V), which indicated that As(III) should be
converted to As (V) in cathodic cell at pH jump from acidity to alkalinity as the electrolysis time was between 27 minutes and 30 minutes.

It is reported that there not only does H₂ evolution from H₂O reduction exist, but also the reduction of O₂ on the cathodic electrode (Ge et al. 2018). The reduction of O₂ to H₂O₂ is far more thermodynamically favorable than the reduction of H₂O to H₂ (Equation (8)), thus decreasing the energy cost for water detoxification.

\[
2H^+ + 2e^- \rightarrow H_2 \quad E_0 = 0V \text{ vs SHE} \quad (8)
\]

It has been demonstrated that the O₂ reduction reaction occurs via two pathways, which are ‘direct’ four-electron reduction and ‘series’ reduction.

The ‘direct’ pathway is a one-step four-electron reduction, as illustrated in Equations (9) and (10), respectively, where no reactive intermediate or product can be generated (Jin et al. 2012).

\[
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E_0 = 1.229V \text{ vs SHE} \quad (9)
\]

\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad E_0 = 0.401V \text{ vs SHE} \quad (10)
\]

In contrast, during the ‘series’ reduction process, O₂ is first reduced to ·O₂, as shown in Equation (11), the reaction is followed by further reduction step to H₂O₂ (in acidic media, Equation (12)) or HO₂ (in basic media, Equation (15)), then reduction to H₂O (Equations (13) and (16)) or disproportionation (Equations (14) and (17)). H₂O₂ easily transforms into HO₂ in alkaline media according to its pKa value of 11.7.

\[
O_2 + e^- \leftrightarrow ·O_2^- \quad (11)
\]

In acidic media:

\[
O_2 + 2H^+ + e^- \leftrightarrow H_2O_2 \quad (12)
\]

\[
H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O \quad E_0 = 1.776V \text{ vs SHE} \quad (13)
\]

\[
2H_2O_2 \leftrightarrow 2H_2O + O_2 \quad (14)
\]

In basic media:

\[
O_2 + H_2O + e^- \leftrightarrow HO_2^- + OH^- \quad E_0 = 0.076V \text{ vs SHE} \quad (15)
\]

\[
HO_2^- + H_2O + 2e^- \leftrightarrow 3OH^- \quad E_0 = 0.878V \text{ vs SHE} \quad (16)
\]

\[
2HO_2^- \leftrightarrow 2OH^- + O_2 \quad (17)
\]

The complicated pathway of the O₂ reduction reaction (ORR) is significantly determined by electrode materials and electrolyte condition, such as pH, solvation, polarization of water, and so on. Different electrode materials (precious metals, nonmetal doped carbon, carbon-transition metal hybrid, and transition metal oxides) have been reported to be able to catalyze ORR in different pathways. O₂ was only stable in concentrated alkaline solutions or aprotic media (Zhang et al. 2009). It was found that more peroxide was generated from O₂ reduction on a graphite cathode, compared with Pt, Ag and indium tin oxide glass, and the production of H₂O₂ on graphite increased with the rise of solution pH in a studied pH range from 2 to 12 (Leng et al. 2006).

In the cathodic cell, H₂ evolution, O₂ reduction, NO₃⁻ reduction (Equations (18) and (19)), As(III) reduction and As(III) oxidation were the main reactions. Before 27 min, the solution still remained strongly acid, As(III) was converted to As(0) and AsH₃ at a rate of 0.405 mg L⁻¹ min⁻¹; it was reported that the reduction of O₂ to H₂O₂ at pH <3 was relatively weak, which could be associated with two side reactions on the carbon cathode, namely, the reduction of H₂O₂ to H₂O and the production of H₂ (Soltani et al. 2013). As a consequence of low yield of H₂O₂ in acid electrolyte, As(III) oxidation to As(V) by H₂O₂ was so weak that it could not be detected before 27 min. The distribution of arsenic species depends on the redox conditions and solution pH; As(III) is easily reduced in acid environment and easily oxidized in alkaline environment (Sharma & Sohn 2013). Between 27 minutes and 30 minutes pH in the cathodic cell jumped from 3.49 to 10.59 (Figure 4(c)), correspondingly the Eh significantly dropped, the reduction rate of As(III) sharply dropped to a very low level. As pH jumped from acidity to alkalinity, the production rate of
H$_2$O$_2$ on the graphite increased dramatically, furthermore, H$_2$O$_2$ might be converted to HO$_2^-$, HO· and ·O$_2^-$ in basic electrolyte (Equations (20) and (21)) (Wang & Wang 2008). The oxidizing powers of HO$_2^-$, HO· and ·O$_2^-$ are all stronger than H$_2$O$_2$. Consequently three quarters of the remaining As(III) in the catholyte was abruptly oxidized to As(V), which was similar to the result of Luo et al. (2015) who found that an alkaline medium was more favorable to the efficiency of phenol degradation than an acid medium with carbon black as cathode.

\[
\text{NO}_3^- + 6\text{H}^+ + 5e^- \leftrightarrow \frac{1}{2}\text{N}_2 + 3\text{H}_2\text{O} \\
E_0 = 0.26V \text{ vs SHE} \tag{18}
\]

\[
\text{NO}_3^- + 9\text{H}^+ + 8e^- \leftrightarrow \text{NH}_3 + 3\text{H}_2\text{O} \\
E_0 = -0.12V \text{ vs SHE} \tag{19}
\]

\[
\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \tag{20}
\]

\[
\text{H}_2\text{O}_2 + \text{HO}_2^- \rightarrow \text{HO}^- \cdot \text{O}_2^- + \text{H}_2\text{O} \tag{21}
\]

After 30 min, As(III) did not convert to As(V) any more, and the ratio of As(III) to As(V) remained 1:3 all the time (Figure 4(a)). This could be ascribed to the significant decomposition of H$_2$O$_2$ in alkaline solution (Wang & Wang 2008). It was reported that H$_2$O$_2$ was relatively stable at pH <9. However, above pH 9, the decomposition rate of H$_2$O$_2$ increased with growing pH, temperature (especially more than 23°C) and reaction time. The self-decomposition of H$_2$O$_2$ at high pH was attributed to two factors: one factor was the catalytic effect of the container walls and the reagent impurities, and the other was that the anion, HO$_2^-$, played an important role in the base catalyzed decomposition of H$_2$O$_2$ (Equation (22)) (Qiang et al. 2002).

\[
\text{H}_2\text{O}_2 + \text{HO}_2^- \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{OH}^- \tag{22}
\]

A voltammogram analysis of the cathode electrode (graphite rod electrode) before and after use for the electrochemical conversion of As(III) for 60 minutes is shown in Figure 5. The oxidation peak from As(0) to As(III) appeared at 0.25 V, which indicated that As(0) was produced from the reduction of As(III) and deposited on the graphite cathode in the cathodic cell.

As the electrolysis time was 60 minutes, the yield of AsH$_3$ which was guided into the AgNO$_3$ solution and detected by the spectrophotometer was 5.999 mg/L (Figure 4(b)). Within the first 30 minutes the yield of AsH$_3$ was 5.060 mg/L, then AsH$_3$ was only increased by 0.939 mg/L within the next 30 minutes. As(0) deposited on the cathode was first cleaned into HNO$_3$ solution and then detected as 0.401 mg/L after 60 minutes (Figure 4(a)) (Bisang et al. 2004; Smirnov et al. 2007; Brusciotti & Duby 2008), As(0) as an intermediate product might be bonded by H* to transform into AsH$_3$. Thus, it was concluded that the main reduction product on the graphite cathode was AsH$_3$, which was similar to the results of Bejan & Bunce (2003); the reduction reaction of As(III) existed in the whole rising pH range from acidity to alkalinity, and the yield of reduction product declined with the ascending pH, which was the same as the results of Smirnov et al. (2007) and consistent with the pourbaix (Eh-pH) diagram of arsenic species.

The evolution of arsine was closely related to the reduction of H* and the preformed As(0) (Cao et al. 2012). The bond energy of the hydrogen molecule was about 435 kJ/mol, while that of two As-H bonds was about 393 kJ/mol, so the hydrogen molecule was not likely to break down to two H atoms and then bond with an As atom. The nascent hydrogen (H*) from the reduction of H$_2$O (Equation (25)) might be bonded covalently to As atoms (Equation (24)) to produce AsH$_3$ (Equation (26)).

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 \uparrow + 2\text{OH}^- \tag{23}
\]
H₃AsO₃ + 3e⁻ → As + 3OH⁻  
(deposited on the cathode)  

H₂O + e⁻ → H⁺ + OH⁻  

As + 3H⁺ → AsH₃↑  

The relationship between the generation percentage of As(0), AsH₃ or As(V) which were all from electrochemical conversion of As(III) and the current efficiency in cathodic cell is shown in Figure 6. As the electrolysis time was between 27 and 30 min, pH in the cathodic cell suddenly jumped from acidity to alkalinity, accompanied with the majority of the remaining As(III) converted to As(V) for an instant, and the current efficiency of As(III) into As(V) reached a maximum of 15.8%.

The As(III) transformation in cathodic cell with pH less than 1.5

The As(III) transformation in the cathodic cell with pH adjusted below 1.5 is shown in Figure 7. The Eh measured was −150 mV, As(III) was mainly converted to arsine gradually, with trace As(0) as intermediate products; after 110 min, As(III) no longer existed, and no As(V) was detected during the whole process. As(III) was oxidized with more difficulty in acid solution than that in basic media (Sharma & Sohn 2006), a high proton concentration in acid solution promoted H₂ evolution and reduced the current efficiency (Qiang et al. 2002), and the reduction of oxygen to H₂O₂ was relatively weak in acid solution compared with that in basic solution (Leng et al. 2006). As a result, the conversion rate from As(III) to As(V) by H₂O₂ was very low and not detectable in the solution with quite high initial As(III) concentration of 40 mg/L.

The transformation of As(III) at low constant voltage

To contrast the conversion pathways of As(III) in cathodic cell at high and low voltage, 1.0 V of low voltage was imposed to electrolyze As(III) in an anode-cathode divided electrolytic tank. 100 ml of 0.1 M HNO₃ solution containing 8 mg/L As(III) (pH 1.12, Eh 512 mV) was added to the anodic cell and the cathodic cell respectively. As(III) was completely oxidized into As(V) in the anodic cell on the 8th day (Figure 8(a)). In the cathodic cell As(III) was completely converted into As(V) on the 37th day (Figure 8(b)), and the conversion process obeyed the zero-order kinetics equation with 0.206 mg L⁻¹d⁻¹. Compared with 40.0 V of high voltage, the sum of As(III) and As(V) remained unchanged in the cathodic cell, indicating that at 1 V the cathode failed to achieve the potential of arsenic reduction and oxidation could still occur in the cathodic cell. pH in the cathodic cell rose to 1.37 on the 38th day. The high current density might give rise to numerous side reactions including a direct four-electron reduction reaction of O₂, H₂ evolution, or a decomposition reaction of H₂O₂ on the surface of the carbon cathode. These side reactions would compete
with the dominant two-electron reduction of O₂ and hinder the generation, accumulation and transformation of H₂O₂ (Lin et al. 2019). Although the generation speed of H₂O₂ from O₂ reduction on a graphite cathode in acid solution was weak at low voltage of 1.0 V (Leng et al. 2019), the generation efficiency of H₂O₂ was higher than that at high voltage, which caused As(III) to be slowly oxidized into As(V) in the catholyte with 8 mg/L total arsenic.

The Eh of the original As(III) solution was 512 mV. As 1.0 V voltage was imposed, the Eh of the anolyte gradually rose at first, then remain unchanged at 1,100 mV after 8 d; the Eh in the cathodic cell also increased at the beginning, then kept the same at 600 mV after 12 d. The generation of H₂O₂ with low yield from O₂ reduction reaction in the pH range from 1.12 to 1.37 might cause higher Eh value in the catholyte than that in the original As(III) solution.

CONCLUSIONS

The electrochemical conversion process and form of As(III) at different voltages and pH was explored in a separated oxidation and reduction environment which was provided by a bi-electrolytic tank separated by a salt bridge. In the anodic compartment, 30 ml of 40 mg/L As(III) on Pt electrode at 40.0 V voltage was completely oxidized into As(V) before 24 min at the speed of 1.558 mg L⁻¹ min⁻¹ by HPLC-ICP-MS. In the cathodic compartment, As(III) was mainly reduced to arsine with As(0) as intermediate on a graphite cathode at the speed of 0.405 mg L⁻¹ min⁻¹ before 27 min. Between 27 minutes and 30 minutes, pH in the cathodic cell jumped from acidity to alkalinity, three quarters of the remaining As(III) in the cathodic cell was transformed into As(V) suddenly. After 30 min, As(III) was not converted to As(V) in the alkaline catholyte, meanwhile the reduction of As(III) in the alkaline catholyte became extremely weak. As pH in cathodic tank was adjusted to keep it acid, As (III) was eventually converted to arsine. Compared with 40.0 V of high voltage, at 1.0 V the cathode failed to achieve the potential of As(III) reduction and As(III) was completely oxidized to As(V) very slowly in the catholyte in the pH range from 1.12 to 1.37. An Eh-pH track diagram of an arsenic containing catholyte on a graphite cathode was produced.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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