1 **Uranium reduction on magnetite:**
2 **Probing for pentavalent uranium using electrochemical methods**

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Abstract

Pentavalent uranium is generally treated as an unstable intermediate when uranyl, U(VI)O_2^{2+} , is reduced to U^{4+} . However, mineral surfaces have been shown to stabilize pentavalent uranium, thus hindering further reduction (Ilton et al., 2005, 2010). The subject of this study is to identify the kinetic pathways that lead to U(V)O_2^+ being a metastable species. Electrochemical methods provide an *in situ* approach for the investigation of the intermediate reaction of U(V)O_2^+ on the surfaces of magnetite. Redox reactions of uranyl ions on particulate ($\sim 3 \mu\text{m}$) and bulk magnetite surfaces were investigated using cyclic voltammetry and potential step chronoamperometry using cavity microelectrodes and bulk (planar) mineral electrodes. The estimated redox potentials are consistent with the standard redox potential of $\text{UO}_2^{2+}/\text{UO}_2^+$, indicating UO_2^{2+} is first reduced to UO_2^+ on the surfaces of both powder and bulk magnetite. The one-electron reduction of UO_2^{2+} to UO_2^+ was further confirmed by directly measuring the number of electrons transferred during the reduction process on the bulk magnetite electrode. Based on the charge conservation analysis and the positive correlation between the pH and the peak current for the UO_2^+ transformation to UO_2^{2+} , the peak corresponding to the oxidation of U^{4+} to UO_2^{2+} was assigned in the voltammograms of particulate magnetite. The presence of U^{4+} indicates that the disproportionation of UO_2^+ ($2 \text{ U(V)} \leftrightarrow \text{U(IV)} + \text{U(VI)}$) is occurring on the surface of particulate magnetite within the timeframe of the experiment. The lack of a peak for U^{4+} in voltammograms for bulk magnetite suggests that the rate of the UO_2^+ disproportionation reaction is slower on bulk magnetite than that on particulate magnetite. The catalytic property of particulate magnetite surfaces on the disproportionation reaction is explained by its ability to adsorb and desorb protons, which could facilitate the proton-coupled disproportionation reaction of UO_2^+ . This increased catalytic activity and related adsorption and desorption kinetics of protons may be related to the increased number of under-coordinated surface sites near step edges on the magnetite powder.

1. Introduction

Hexavalent uranium exists as the soluble uranyl ion (UO_2^{2+}) in aqueous environments but can be reduced to soluble U(V)O_2^+ and to relatively insoluble U(IV) species. The change in oxidation state has a significant influence on the solubility of uranium, and therefore, the mobility of uranium in the environment. Magnetite (Fe_3O_4) is a common naturally-occurring iron oxide, and it is also found as a corrosion product of iron under anoxic conditions, such as in zero-valent iron permeable reactive barriers used for the remediation of uranium contaminated ground water and in steel canisters used for the nuclear waste storage (Cornell and Schwertmann, 1996; Gu et al., 1998; Morrison et al., 2001; Dodge et al., 2002; Rovira et al., 2007; Dickinson and Scott, 2010). Numerous studies have identified the retention of uranium through heterogeneous reduction of UO_2^{2+} to U(IV) on the surface of magnetite (e.g., Scott et al., 2005; Gorski and Scherer, 2009; Gorski et al., 2010; Gorski and Scherer, 2010;). Solid U(IV) species formed on magnetite surfaces have been ascribed to the reduction of UO_2^{2+} by transferring electrons from Fe(II) in the magnetite or by other electron donors in solution. In the latter case, the shuttling of electrons between reducing agents and adsorbed UO_2^{2+} is facilitated by the highly conductive surface of magnetite (Becker et al., 2001; Missana et al., 2003; Rosso and Becker, 2003; Renock and Becker, 2010; Gorski et al., 2012; Latta et al., 2012; Singer et al., 2012a; Singer et al., 2012b). The two-electron reduction of UO_2^{2+} to U^{4+} is more energetically favored than the one-electron reduction of UO_2^{2+} to UO_2^+ based on standard reduction potentials (*i.e.*, $E^0_{\text{U(VI)/U(IV)}} = 0.070 \text{ V}$, $E^0_{\text{U(VI)/U(V)}} = -0.135 \text{ V}$, all potentials in this manuscript are with respect to the Ag/AgCl , saturated KCl , 0.197 V vs. NHE) (Morris, 2002; Konings et al., 2006). However, direct reduction from UO_2^{2+} to U^{4+} is kinetically hindered due to the significant change between the structures of the reactant and the product, where the UO_2^{2+} exists as the stable linear uranyl molecule with the short U=O bond (Burns, 1999). The more facile pathway to produce U^{4+} is one in which UO_2^{2+} is first reduced to UO_2^+ , followed by the formation of U^{4+} through the rapid disproportionation of two UO_2^+ ions (Eq. (1-3)) (Kern and Orlemann, 1949; Steele and Taylor, 2007).

The UO_2^+ disproportionation reaction starts with the formation of a UO_2^+ dimer through cation-cation interactions, followed by a coupled reaction involving both electron transfer and protonation of the axial oxygen of the donor UO_2^+ ion (Eq. (1)) (Steele and Taylor, 2007; Fortier and Hayton, 2010). Eq (2) considers the dominant species of U^{4+} under acidic conditions to be $\text{U}(\text{OH})_3^+$ (hydrolysis step) (Neck et al., 2001). The overall reaction is given by Eq (3). The measured rate constant for UO_2^+ disproportionation is $3.4 \times 10^2 \text{ M}^{-1} \cdot \text{s}^{-1}$ in acidic perchlorate solution (Ekstrom, 1974). Thus, UO_2^+ is generally treated as an unstable intermediate species. However, the presence of stabilized UO_2^+ has been identified in abiotic and biological reduction experiments, in corrosion studies of UO_2 , in the mineral wyartite ($\text{CaU}^{5+}(\text{UO}_2)_2\text{O}_4(\text{CO}_3)(\text{OH}) \cdot 7\text{H}_2\text{O}$) and in synthetic actinide compounds, suggesting that the UO_2^+ ion is stabilized under specific conditions (Burns and Finch, 1999; Goldik et al., 2004; Sunder et al., 2004; Ilton et al., 2005; Renshaw et al., 2005; Broczkowski et al., 2007; Graves et al., 2008; Graves et al., 2009; Ilton et al., 2010; Heming He, 2012; Ilton et al., 2012; Razdan et al., 2012). Possible reasons for the stabilization of U(V) are sorption to mineral surfaces, incorporation into the mineral structure and formation of a uranate-type coordination environment for UO_2^+ , and the slow rate of protonation during the coupled electron transfer-protonation reaction in Eq. (1) (Ilton et al., 2005; Skomurski et al., 2011; Ilton et al., 2012; Wander and Shuford, 2012). The presence of the stabilized pentavalent uranium is of great importance to the fate of uranium in the environment. If uranium can form solid phases in the pentavalent state, this will lead to a new type of “sink” that is based on a reduction and precipitation mechanism, thus reducing the mobility of uranium in the environment (Belai et al., 2008).

In previous studies, uranium oxidation states on mineral surfaces were characterized under various environmental conditions using *ex situ* methods, such as X-ray photoelectron spectroscopy (XPS), and *in situ* methods (*e.g.*, X-ray absorption near edge spectroscopy, XANES) (Sturchio et al., 1998; Reeder et al., 2001; Rakovan et al., 2002; Elzinga et al., 2004; Antonio and Soderholm, 2006; Komlos et al., 2008; Luo et al., 2009; Schindler et al., 2009; Ilton and Bagus, 2011; Singer et al., 2012a; Wang et al., 2013). While such approaches allow for the determination of the structure and chemical state, it is difficult to control the redox potential during the experiment precisely. The advantage of using electrochemical methods is that redox

conditions close to the electrode-liquid interface can be controlled by the applied potential. Such electrochemical methods have been used to study environmental surface reactions by employing electrodes made of metallic or semiconducting materials (Castro, et al., 1996; Scherer et al., 1997; Nurmi et al., 2005; Nurmi and Tratnyek, 2008; Latta et al., 2012; Renock et al., 2013). In electrochemical experiments, the rate of the redox reaction(s) of uranium species can be driven by the applied potential across the electrode-liquid interface. The flow of electrons in and out of the electrode surface is recorded as current and the mechanisms of redox reactions can then be extracted based on the current-potential relationship. Renock et al. (2013) first identified redox peaks of the $\text{UO}_2^{2+}/\text{UO}_2^+$ couple on semiconducting mineral powders. Such electrochemical studies require high conductivity between mineral particles in the packed bed as well as between particles and the underlying working electrode (*i.e.* Pt wire, the current collector). Thus, in this study, the stability and magnitude of the current signal in cyclic voltammograms of the cavity microelectrode was enhanced by mixing a conductivity enhancer, graphite, into the magnetite particles. Moreover, not only voltammograms of the surface of particulate magnetite but also those of bulk magnetite were investigated, in which the known surface area of the bulk mineral electrode allows determination of the number of electrons transferred in the reduction of UO_2^{2+} . Furthermore, the particle size has been shown to control the density of the defect sites on the magnetite surface, and the surface defect density of nano and micro-particulate magnetite is likely to be higher than that of bulk magnetite (Sun et al., 1998; Peng et al., 2008; Petitto et al. 2010). We hypothesize that differences in defect density on the surface of magnetite may lead to different redox mechanisms (kinetic pathways) for the uranium reduction process. The objective of this study is to identify and compare the kinetic pathways for UO_2^{2+} reduction on the surfaces of particulate and bulk magnetite using electrochemical methods. Possible mechanisms regarding the U(V)O_2^+ being a metastable species will be discussed based on the electrochemical results.

2. Materials and Methods

2.1 Magnetite powder cavity microelectrode

The cavity microelectrode contains a Pt wire, sealed inside a glass tube, which has been etched in *aqua regia* to create the cavity. The diameter of the cylindrical cavity is determined by the diameter of the Pt wire, and the depth of the cavity is controlled by the etching time. The temperature of the *aqua regia* solution is controlled between 70-80 °C. The electrode was

repeatedly checked using optical microscopy every 20-30 min until the desired depth ($\sim 30\ \mu\text{m}$) was obtained. Details on preparing the cavity microelectrode are described elsewhere (Cha et al., 1994; Cachet-Vivier et al., 2001; Athouel et al., 2012; Renock et al., 2013). Magnetite was obtained from Mineville, New York (Ward's Science, USA), and crystals with the lowest number of visible inclusions were selected for energy dispersive X-ray analysis (EDS) using a SEM (Philips XL30). Subsequently, magnetite crystals without evident impurity elements on the EDS spectrum were selected for the experiments. Magnetite powder was obtained by grinding the magnetite crystals using an agate mortar and pestle under atmospheric conditions immediately prior to the experiment. In order to improve the conductivity between magnetite grains, magnetite was mixed with graphite powder (10 wt.%), the latter being ground from a graphite rod used for conductive coating of SEM samples, using mortar and pestle. SiO_2 powder, which is used in the mixed powder containing SiO_2 and graphite for testing the current contribution from graphite, is ground from a SiO_2 crystal in the mortar. Both magnetite and SiO_2 powder had a similar average grain size of $3\ \mu\text{m}$ from SEM image analysis. The experiments found that a few seconds of sonication in deionized (DI) water can remove most of the powder packed inside the cavity. After each experiment, three types of solution were used to clean the electrode, that is, DI water, 0.01M HNO_3 , and ethanol. The electrode was sonicated first in DI water to remove the magnetite particles and then in 0.01M HNO_3 solution and then in DI water again to remove nitric acid and finally in ethanol. Each sonication step in respect solutions lasts about 10s. The electrode was then dried in air before packing with new powder.

2.2 Bulk magnetite electrode

The magnetite samples from Mineville N.Y. have octahedral parting from which the (111) surface can be obtained. The samples were polished down to the thickness of 1.5 mm using $6\ \mu\text{m}$, $3\ \mu\text{m}$ and $1\ \mu\text{m}$ diamond sand papers, successively. The polishing work was under atmospheric conditions on dry sand papers, and then the magnetite samples were sonicated in deionized water, acetone and ethanol. Cu wire was then connected to one side of the magnetite crystal using silver paste and sealed in epoxy, such that only one side of the polished surface was exposed to the solution for reaction. The same bulk magnetite electrode was used for all electrochemical experiments. Fresh surfaces were obtained by polishing and cleaning methods described above immediately before the experiment. The geometric area of the magnetite electrode was $0.13\ \text{cm}^2$.

2.3 Electrochemistry experiments

A computer-controlled potentiostat (Princeton Applied Research Model 263A using *PowerSuite* software) was used to control the voltage applied to the magnetite working electrode with respect to the Ag/AgCl (saturated KCl) reference electrode, as well as to measure the current that passed between the working electrode and a Pt counter electrode. The working electrode was either the cavity microelectrode (powder magnetite) or the bulk electrode (*i.e.* magnetite (111) surface). Cyclic voltammetry experiments were started from the open circuit potential (equilibrium potential on the working electrode) and scanned first to more positive potentials at a scan rate of 50 mV/s until the switching potential was reached (unless otherwise stated). The potential scan was repeated for 10 to 20 cycles.

The potential step chronoamperometry method provides a unique approach to directly calculate the number of electrons transferred in the redox reaction. In this method, instead of ramping the potential, the voltage was held at a constant value and the current was measured as a function of time. A voltage of -1.0 V was applied to the bulk magnetite electrode, which is 0.865 V less than the standard redox potential of the $\text{UO}_2^{2+}/\text{UO}_2^+$ couple ($E^0 = -0.135$ V). Being significantly below the standard reduction potential minimizes the energy barrier for the electron transfer process, and the reduction kinetics of UO_2^{2+} is mainly controlled by diffusion, that is, the current is determined by how fast the UO_2^{2+} can be transported to the electrode surface through diffusion. The relationship between the current and the time for such a reaction is described in the Cottrell equation (Bard and Faulkner, 2001):

$$I(t) = \frac{nFAD_0^{1/2}C_0}{\pi^{1/2}t^{1/2}} \quad (4)$$

where I is the current in A, n is the number of electrons transferred per redox change (*i.e.*, if the oxidation state changes by 1, n is 1), F is the Faraday constant $96485.3365 \text{ C}\cdot\text{mol}^{-1}$, A is the reactive surface area in cm^2 , D_0 is the diffusion coefficient of uranyl in sulfate solution ($4.0 \times 10^{-6} \text{ cm}^2/\text{s}$) (Awakura et al., 1987), C_0 is the initial concentration of UO_2^{2+} ions in $\text{mol}\cdot\text{L}^{-1}$ and t is the time in s.

A solution containing 0.1 M ferrocyanide, which was used to test the effectiveness of the cavity microelectrode, was prepared by dissolving $\text{K}_4\text{Fe}(\text{CN})_6$ (Acros Organics) in deionized

water. Uranyl nitrate hexahydrate crystals $[\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ (International Bio-Analytical Industries, Inc.) were dissolved in the deionized water to prepare the uranyl nitrate stock solution. Uranyl solutions of different concentrations used in experiments were then prepared by adding certain amounts of uranyl nitrate stock solution into 0.1 M Na_2SO_4 (Fisher Scientific) as the background electrolyte. The Fe(II) solution was prepared by dissolving $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ (Acros Organics) in deionized water (degassed by Ar). The pH of the solution was adjusted using 0.1 M solutions of either H_2SO_4 or NaOH and measured using the Orion 111A pH meter. All solutions were degassed with Ar for at least 30 min prior to experiments. All voltammograms plot negative current for the cathodic scan and positive current for the anodic scan.

3. Results and Discussion

3.1 Testing the cavity microelectrode using the ferro/ferricyanide redox couple

Although cavity microelectrodes have been used for studying the reactivity of a variety of powders, it is possible that direct reactions (*i.e.*, without the involvement of the mineral surface) between the Pt wire, which acts as a current collector at the base of the cavity, and redox-active species in solution can occur (Athouel et al., 2012). In addition, poor conductivity of powder materials can result in low current signal, making it difficult to identify the redox peak from the background current. By reproducing the reversible one-electron reaction of the $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ couple ($E^0 = 0.363\text{V}$ vs. Ag/AgCl in 0.1M HCl) (Bard and Faulkner, 2001), the effectiveness of the cavity microelectrode was evaluated. Significant enhancement of the current signal was observed by adding 10 wt.% graphite powder into the magnetite. The graphite acts as a conductivity enhancer by decreasing inter-particle resistance. The faradaic currents from the ferro/ferricyanide redox reactions on graphite alone are relatively small as compared with those for magnetite and graphite (Fig. 1a). Voltammograms of magnetite and magnetite mixed with graphite powder show higher background current than the other two voltammograms, which is due to the capacitive current from charging the double layer of graphite and magnetite. The enhanced peak-current signal (Fig. 1a, voltammogram of magnetite + graphite) above the background capacitive current is 2.2 times higher than the sum of the two voltammograms of magnetite and SiO_2 + graphite together (Fig. 1a, SiO_2 powder with the similar grain size of the magnetite powder is served as a non-conductive media to replace the volume of magnetite). This result indicates that the graphite itself is not the dominant reactive surface. Instead, graphite

provides a highly conductive medium that can conduct electrons first from one grain to another and subsequently to the current collector (Pt wire) efficiently (Fig. 1b). The peak separation is a direct indication of the reversibility of a redox reaction. In a reversible redox reaction, the kinetics is controlled by diffusion rather than charge transfer on the metallic electrode or the charge depletion/accumulation in the conduction band of the semiconducting electrode. In this reversible case, the theoretical peak separation is 59 mV for a single electron transfer process (Bard and Faulkner, 2001). The peak separation on the voltammogram of the ferro/ferricyanide redox couple measured by the cavity microelectrode loaded with mixed magnetite and graphite powder (Fig. 1a, voltammogram of magnetite + graphite) increases from 68 mV in the first scan cycle to 161 mV in the 20th cycle. The peak separation is 115 mV on the metallic Pt electrode (Fig. 1a, empty cavity), indicating that magnetite has minor influence on the reversibility of the redox behavior. The reason for the increased peak separation with the number of the scan cycles on the voltammogram of magnetite + graphite is still not clear. By measuring the peak current value, the surface area of the mixed magnetite with graphite powder inside the cavity was estimated to be 3600 μm^2 according to the equation for the reversible one-electron redox couple between ferro/ferricyanide as compared with the geometric area of the top surface of the Pt wire, which is only 1963 μm^2 as calculated from the cavity diameter (Bard and Faulkner, 2001). Similar tests in uranium solution were done (see section 3.2), and the conductivity between magnetite grains was also improved by adding graphite powder.

The I-E reproducibility of the cavity microelectrode was assessed by measuring the voltammogram of ferro/ferricyanide on magnetite + graphite for 10 freshly prepared electrodes. The uncertainty of the peak current value was found to be $\pm 0.02 \mu\text{A}$ (for absolute peak heights typically ranging from 0.5 to 1.0 μA). Details regarding the reproducibility tests are described in the appendix.

3.2 Redox reactions of the magnetite powder in background electrolyte

Cyclic voltammograms of cavity microelectrodes in 0.1 M Na_2SO_4 solution exhibit the highest current signal in the electrode packed with mixed magnetite and graphite powder (Fig. 2a, magnetite + graphite). The current measured during cyclic voltammetry of semiconducting materials results from the capacitive currents (*i.e.*, currents resulting from charging/discharging of the electric double layer) and from redox reactions on the electrode surface (*i.e.*, faradaic

currents). Faradaic currents include reactions of the electrode material and reactions between the electrode and dissolved species in the electrolyte (Wu et al., 2003). White et al. (1994) assigned the two half-cell reactions on magnetite to the cathodic dissolution of magnetite (Eq. (5)) and the oxidation of magnetite to maghemite (Eq. (6)), respectively.

The cathodic current (*i.e.*, currents associated with the cathodic dissolution of magnetite) increase continuously when the potential is scanned negatively (*i.e.*, cathodic), which is in contrast to the relatively flat anodic current curve (Fig. 2a, magnetite + graphite). The flat anodic current is attributed to the formation of maghemite, a relatively unreactive passivation layer that prevents further oxidation of the surface (White et al., 1994). However, these peak assignments are not consistent with voltammetric peaks observed in the present study.

Magnetite cyclic voltammetry shows two coupled redox peaks (identified as C1/A1 and C2/A2 in Fig. 2a) on top of the background current, which becomes more pronounced when the pH of the solution is lowered (Fig. 2b). Cyclic voltammograms using the graphite powder and the empty cavity microelectrode were also collected, and the absence of these two redox peaks (C1/A1 and C2/A2) on graphite and Pt indicates the redox reactions were specific to magnetite (Fig. 2a, SiO₂ + graphite and empty cavity). For the C1/A1 couple, the anodic peak current A1 is 3.8 times higher than that of C1, indicating differences in the kinetics of the reduction and the oxidation process. The peak separation is of 226 mV, suggesting the irreversibility of the reaction. In order to find the redox couple corresponding to the C1/A1 peaks, a series of voltammograms were collected in solutions with different concentrations of Fe²⁺ and SO₄²⁻. Peak currents for the C1/A1 couple increase with an increase in free Fe²⁺ concentration (Fig. 2a, inserted graph), but not SO₄²⁻ (data not shown), suggesting that the C1/A1 couple is related to the redox reaction of the free Fe²⁺/Fe³⁺ in the solution on the surface of magnetite. Although the midpoint potential ($E_{1/2} = (E_{A1} + E_{C1})/2$) can be distorted by irreversible peak behavior, it is used as a first approximation for the formal redox potential of the C1/A1 couple. The midpoint potential of the C1/A1 couple is approximately 0.31 V (Eq. (7)). This formal potential does not represent the equilibrium potential of a magnetite surface, but is specific for the redox reaction of

free Fe^{2+} from solution on a magnetite surface. To our knowledge, this midpoint potential does not match exactly with known redox reactions of free ions of $\text{Fe}^{2+}/\text{Fe}^{3+}$ (0.574V vs. Ag/AgCl). Fe^{2+} can be released into solution from the magnetite electrode during the cathodic scan and then oxidized back to Fe^{3+} corresponding to the peak A1. The peak current of the C1/A1 redox couple decreases with increasing the pH of the solution, and the peak position of A1 shifts to the left from 0.41 V to 0.35 V when the pH is increased from 3.44 to 4.50 (Fig. 2b). This obeys the pH-dependent Nernst relation ($E = E^0 - 0.0592 \text{ pH}$, at 25 °C) (Bard and Faulkner, 2001), indicating a proton-coupled redox reaction. With the consideration of the acidic pH condition that constrains the dominant Fe^{3+} species to be $\text{Fe}(\text{OH})^{2+}$ (based on speciation calculations by *Visual MINTEQ*), the proposed reaction for the C1/A1 redox couple can be written as:

The redox couple C2/A2 exhibits peaks separated by 83 mV from each other, suggesting relatively reversible behavior. The peak current decreases with the increase of the solution pH and is independent of the concentration changes of Fe^{2+} and SO_4^{2-} in solution; thus, it was assigned to H^+ adsorption/desorption reactions as:

which has also been identified on voltammograms of other conductive oxides, such as IrO_2 and SnO_2 (Locatelli et al., 2011).

3.3 Double anodic peaks and the UO_2^{2+} disproportionation on magnetite powder

Additional peaks appear (see C3/A3 in Fig. 3a) when uranium is added to the background electrolyte. The peak current of C3 and A3 (i_{pc3} , i_{pa3}) both show a positive linear correlation with the UO_2^{2+} concentration (Fig. 3b), indicating that the C3/A3 couple is related to UO_2^{2+} redox reactions on magnetite. The cathodic and anodic peak current on the voltammogram of magnetite in the ferrocyanide solution (Fig. 1a, magnetite) have similar absolute values with a peak separation of 115 mV, indicative of a quasi-reversible one-electron reaction. On the contrary, the anodic peak current i_{pa3} (A3) in the UO_2^{2+} solution (Fig. 3a, b) is more than two times higher than the cathodic i_{pc3} (C3) and the peak separation is as large as 176 mV. The large differences between the shape of the cathodic and anodic peaks observed in the UO_2^{2+} solution

can be caused either by significant differences in the kinetics between the reduction and the oxidation half reactions of the uranyl or can be the result of coupled homogeneous reactions (*e.g.*, UO_2^+ disproportionation). The calculated midpoint potential (-0.085 V) of the C3/A3 peak on the powder magnetite is close to the redox potential of $\text{UO}_2^{2+}/\text{UO}_2^+$ ($E_{\text{U(VI)/U(V)}} = -0.135$ V, 0.05 V in difference) in comparison with 0.070 V for the $\text{UO}_2^{2+}/\text{U}^{4+}$ redox couple (0.155 V in difference). In addition to the primary peak C3/A3 caused by the $\text{UO}_2^{2+}/\text{UO}_2^+$ couple, the peak A4 at 0.438 V also increases with increasing the UO_2^{2+} concentration. A similar peak (A4) at 0.45 V was identified on the cyclic voltammogram of hematite powder in the UO_2^{2+} solution (Renock et al., 2013). In order to find redox reactions corresponding to the peak A4, the charge transferred under the cathodic and anodic peaks on the voltammograms in Fig. 3a was calculated based on Eq. (9):

$$Q = \int_{E1}^{E2} \frac{I}{\nu} dE \quad (9)$$

Q is the charge in coulombs (C), $E1$ and $E2$ are the two potentials, which define the scan range in V, I is the current in A and ν is the scan rate in V/s. All integrated charges of the cathodic (C3) and anodic (A3 + A4) half cycle on voltammograms in Fig. 3a had similar values (Fig. 3c) as a function of the UO_2^{2+} concentration. The similar amount of charge transferred in the single cathodic peak and double anodic peaks obeys the conservation of charge, indicating the conservation of the amount of uranium species reduced and oxidized in a complete redox cycle. Therefore, the peak A4 has to be part of the uranyl redox reaction and is most likely caused by the oxidation of the disproportionation product U^{4+} (Eq. (1)) back to UO_2^{2+} (section 3.3 also proves that the disproportionation reaction occurred during the experiment). If the reduced UO_2^+ was stable in solution, it would be oxidized back to UO_2^{2+} in the reverse anodic scan, and the charge flow under the primary redox peaks (C3/A3) would have a similar value and no additional peak (A4) would be found in the voltammogram. However, the UO_2^+ generated in the reduction step is not stable, and part of the UO_2^+ disproportionate into UO_2^{2+} and U^{4+} (Eq. (1)). The extra UO_2^{2+} flux would be generated continuously towards the electrode surface through UO_2^+ disproportionation, which explains the steady-state cathodic current observed in C3 (Fig. 3a). Note, U^{4+} is not oxidized to UO_2^+ first and then to UO_2^{2+} , because if it was, a two-step oxidation reaction ($\text{U}^{4+} \rightarrow \text{UO}_2^+ \rightarrow \text{UO}_2^{2+}$) resulting in two anodic peaks of similar peak current would be observed instead of the single peak (A4, $\text{U}^{4+} \rightarrow \text{UO}_2^{2+}$) found here. Particularly, the

position of peak A4 ($\text{U}^{4+}/\text{UO}_2^{2+}$) is very close to the potential of the peak A1, which was previously assigned to the oxidation of Fe^{2+} to Fe^{3+} , and the reason for such a similar peak position is still not clear. Experimental studies have found close redox potentials between the Fe(II)/Fe(III) -containing (hydr)oxides and the U(VI)/U(IV) redox couples under common groundwater conditions (Ginder-Vogel, et al, 2006). In addition, similar peak positions on the voltammogram also indicate that the two species (U^{4+} and Fe^{2+}) require a similar potential to extract electrons from their highest occupied molecular orbital (HOMO) to the conduction band of magnetite in order to be oxidized. Thus, it is possible that U^{4+} and Fe^{2+} species have very similar U 5*f* and Fe 3*d* energy levels, resulting in the same peak potential on the voltammograms.

Current contributions from the UO_2^{2+} redox reactions on graphite powder, Pt wire electrode, magnetite powder and the powder containing magnetite mixed with graphite were analyzed (Fig. 3d). Adding graphite into the magnetite powder enhanced the current signal from redox reactions with uranium (Fig. 3d, magnetite + graphite). In particular, the voltammogram of the graphite powder (Fig. 3d, SiO_2 + graphite) has a similar peak pattern as compared with the voltammogram of magnetite + graphite (primary redox peaks (C3/A3) and the side peak (A4)), indicating that the UO_2^{2+} can also disproportionate on the graphite powder. However, the current from graphite alone is 4.5 times lower for the primary redox peaks (A3) and is 2.5 times lower for the side peak (A4) as compared to the current on the voltammogram of magnetite + graphite, indicating that the current contribution from UO_2^{2+} redox reactions is mainly from the reaction on magnetite.

3.4 Proton-facilitated UO_2^{2+} disproportionation

The reduction of UO_2^{2+} to UO_2^{+} and the subsequent UO_2^{+} disproportionation on the magnetite powder can also be confirmed by studying the anodic half reaction in solutions of different pH. The voltammetric peak A3 exhibited two different trends when the pH was increased. In the first trend, the height of the peak A3 ascribed to the oxidation of UO_2^{+} to UO_2^{2+} increased when pH was increased from 3.36 to 3.88 (Fig. 4a, process 1). Since the UO_2^{+} disproportionation involves H^{+} (Eq. (1)), decreasing the H^{+} concentration by increasing pH suppresses the consumption rate of UO_2^{+} through disproportionation, such that more UO_2^{+} would be saved in the reverse anodic scan, which explains the increasing peak current of A3 (Fig. 4a, process 1, A3 is due to UO_2^{+} to UO_2^{2+}) with the increase of pH. This current-pH relationship verifies that the redox reactions of

C3/A3 were not the two-electron reaction between the $\text{UO}_2^{2+}/\text{U}^{4+}$ couple. If the cathodic peak C3 resulted from the reduction of UO_2^{2+} to U^{4+} , then the anodic peak A3 would be caused by the oxidation of U^{4+} to UO_2^{2+} . Decreasing the H^+ concentration by increasing the pH, less U^{4+} is generated during the reduction because this reaction involves the participation of H^+ (Eq. (10)). Therefore, a decrease in the A3 peak current, which would be caused by oxidation of U^{4+} to UO_2^{2+} , instead of the observed increase, would be found in the voltammogram.

With the continued increase of the pH from 4.40 to 4.81, the peak height of A3 starts to decrease quickly (Fig. 4a, process 2). The increase in pH from 4.40 to 4.81 influences the concentration of the dominant species, $\text{UO}_2\text{SO}_{4(\text{aq})}$ in solution according to thermodynamic calculations using the *Visual MINTEQ* software, where the total amount of soluble uranium species starts to decrease at pH 4.0 (Fig. 4b). Thus, the decrease in the amount of the redox-active species is likely to occur in process 2 showed in Fig. 4a, which results in the decrease of peak current A3. In addition, peak A4 decreases continuously with the increase of pH, which is due to the decrease of the amount of U^{4+} generated by disproportionation at higher pH. This is consistent with the previous assignment of peak A4 to the oxidation of U^{4+} to UO_2^{2+} .

3.5 Stabilized UO_2^+ on the surface of the bulk magnetite electrode

On the bulk magnetite electrode, cathodic and anodic peaks related to uranyl redox reactions have a more similar peak shape and similar peak current heights when compared to voltammograms of the magnetite powder. The shape of the voltammogram on the bulk magnetite electrode gradually stabilized with increasing the number of scan cycles (Fig. 5a), which was not observed on the voltammogram of the powder magnetite (Fig. 3a). The cathodic charge density dropped quickly in the first two cycles and approached the stable state in the following scan. On the contrary, the anodic charge density increased with scan cycle and gradually approached the charge density of the cathodic scan (Fig. 5b). Thus, the ratio of the cathodic and the anodic charge decreased from 2.8 to 1.2 within 12 cycles (Fig. 5b, inserted graph). Comparing with the cathodic current in the background solution (Fig. 5a, dashed line), the tail of the cathodic current density of the last cycle in UO_2^{2+} solution was about $2.1 \mu\text{A}/\text{cm}^2$ less than the current density in the background solution. This is likely due to a decrease in reactive surface area, which may be

caused by adsorption of uranium species generated in the cathodic scan, most likely UO_2^+ to the surface of the electrode as indicated by the absence of the U^{4+} oxidation peak (peak A4, Fig. 3a) in the anodic scan.

The reason for the faster disproportionation of UO_2^+ on the powder magnetite (presence of the side peak A4 caused by the U^{4+} oxidation) than that on the bulk magnetite electrode (absence of the side peak A4) is still not clear. However, when the bulk electrode was applied at a constant potential of -0.6 V for 5 min before the cyclic scan, the first cycle of the voltammogram showed a broad oxidation peak. The new weak peak at 0.17 V was identified only in the first cycle (Fig. 5c. new peak indicated by the arrow), suggesting a long period of polarization before the scan generated other species, which is very likely to be related to U^{4+} . The voltammogram in the second cycle returned back to the baseline current, similar to the redox reaction of $\text{UO}_2^{2+}/\text{UO}_2^+$ found in Fig. 5a. Therefore, it is very likely that the UO_2^+ disproportionation reaction can also occur on the bulk magnetite electrode, but at a much slower rate than on the surface of the powder magnetite.

The inner-sphere UO_2^+ disproportionation mechanism has been proposed by Steele and Taylor (2007) by first forming the UO_2^+ dimer through cation-cation interactions, that is, the oxo-O from one of the $\text{O}=\text{U}(\text{V})=\text{O}$ needs to bond with the uranium atom from another UO_2^+ in order to form the “T” shape configuration, which is then followed by proton-coupled electron transfer at the donor UO_2^+ ion (Nocton et al., 2008; Fortier and Hayton, 2010; Mougel et al., 2010). Thus, the fast disproportionation rate found on the powder magnetite surface could result from the powder surface being able to either promote the $\text{U}(\text{V})$ dimer formation or facilitate the electron transfer from the donor UO_2^+ to the acceptor UO_2^+ . Bulk and powder magnetite have different surface structures, resulting in different defect densities. Petitto et al. (2010) identified two types of oxygen-terminated bulk magnetite (111) surfaces under hydrated conditions in neutral pH. Protonation of the surface O atoms is expected and the redox-active $\text{Fe}^{2+}/\text{Fe}^{3+}$ cations were under the hydrated surface layers. Surfaces of the magnetite particles have higher density of Fe and O defect sites compared to the bulk magnetite surface. Numerous studies, especially studies on magnetite nanoparticles, have showed increased catalytic properties with decrease in grain size (Sun et al., 1998, Peng et al., 2008). One notable difference between the powder and bulk magnetite electrode is that the surface of powder magnetite shows higher reactivity, indicated by

the protonation/deprotonation reaction (Fig. 2a, peak C2/A2) in the background solution, as compared to the relatively smooth voltammogram of the bulk magnetite electrode in the same electrolyte (Fig. 5a, dashed line). The UO_2^+ disproportionation is a proton-coupled electron transfer reaction. Thus, it is possible that the active protonation/deprotonation sites on the surface of the powder magnetite provide the area with higher surface coverage of sorbed protons compare to the bulk surface, which facilitates the UO_2^+ disproportionation (Fig. 5d).

In addition, because of the amount of powder ($\sim \mu\text{g}$) can be loaded to the powder microelectrode is constrained by the size of the cavity, the surface area of the bulk electrode (0.13 cm^2) is larger than that of the powder microelectrode ($\sim 4000 \mu\text{m}^2$). The difference in surface area results in the greater currents observed in the voltammograms of the bulk magnetite electrode. Thus, more UO_2^+ can be generated in the reduction (cathodic scan) by using the bulk magnetite electrode. Although, the rate of the UO_2^+ disproportionation should increase with increasing its concentration, it is possible that if a solubility limit is reached for a U(V)-containing phase, then the UO_2^+ disproportionation will be inhibited. However, the exact mechanism of how the surface of the magnetite powder facilitates UO_2^+ disproportionation and whether there is a formation of stable U(V)-containing phase on the bulk magnetite still need further investigations.

3.6 Fitting the one-electron reduction of UO_2^{2+} on the bulk magnetite electrode

The bulk magnetite electrode was polarized at -1.0 V (vs. Ag/AgCl) for 20 s in background solutions and UO_2^{2+} containing solutions, respectively. The magnitude of the cathodic current decreased exponentially in both solutions with the increase of time (Fig. 6a). The current in the background electrolyte was mainly from charging the double layer of the magnetite and the potential H_2O reduction reaction. The current in the UO_2^{2+} solution is the combination of both reactions on the magnetite in background electrolyte and reactions of the UO_2^{2+} reduction. Thus, larger current magnitude was found in the voltammogram in the UO_2^{2+} solution than that in the background solution. By subtracting the current in the background solution from the current in the UO_2^{2+} solution, the current contribution from the UO_2^{2+} reduction alone can be extracted (Fig. 6a, inserted graph). Based on Eq. (4), the number of electrons n can be fitted to the slope of the data plotted in Fig. 6b. The data point at $t = 1 \text{ s}$ was not fitted because it is off the line of the other data in the range from 2 s to 10 s (if the data at 1 s was involved in the fitting, the slope is

1.0 and the R^2 is 0.97). The reason for the deviation of the data point at one second could be caused by the non-steady state at the very beginning of the experiments. After 10 s, the diffusion profile and the concentration gradient of UO_2^{2+} close to the electrode surface started to be interrupted by the solution convection, which is indicated by the alignment of the data point at 8 μA (Fig. 6b). The diffusion current after 10 s no longer obeys the ideal diffusion process described by the Cottrell equation (Eq. (4)); thus, data collected after 10 s was not used in the fitting. The number of electrons transferred was finally fitted to yield a value of 1.2, which corresponds to the one-electron reduction of UO_2^{2+} to UO_2^+ . Particularly, even at -1.0 V, the reduction pathway of UO_2^{2+} still follows the one-electron reduction to UO_2^+ rather than the two-electron reduction to U^{4+} . In comparison, the two-electron reduction mechanism of transferring electrons from Fe(II) to UO_2^{2+} was proposed by Boyanov et al. (2007). When the dominant Fe(II) species is monomeric Fe(II) at pH 7.5, which can only donate one electron, the reduction of UO_2^{2+} to U(IV) was not found. But rapid reduction to U(IV) was found when the pH was increased to 8.4, where Fe(II) oligomerized to $\text{Fe}(\text{OH})_2$ -like species with the possibility to donate two electrons. However, electrons here were provided by the potentiostat instead of limited by the type of Fe(II) species in the solution. Considering the acidic pH in this work is different from the basic conditions where $\text{Fe}(\text{OH})_2$ -like species donate two-electrons to U(VI), pH may be an important factor on determining the number of electrons transferred in the U(VI) reaction. In general, the fitting result, which is measured by another independent method, confirms that the UO_2^{2+} reduction on magnetite produces pentavalent uranium in current experimental conditions, at least as an intermediate state.

4. Summary and conclusions

Redox reactions of uranyl ions on the surface of powdered and bulk magnetite in the aqueous solutions were investigated using electrochemical methods. Significant enhancement of the current signal from uranium redox reactions was observed by adding graphite powder into the magnetite powder. On the voltammograms of the powder magnetite, the cathodic peak at -0.26 V vs. Ag/AgCl was assigned to the reduction of UO_2^{2+} to UO_2^+ coupled with UO_2^+ disproportionation. The first anodic peak at 0.09 V vs. Ag/AgCl was ascribed to the oxidation of UO_2^+ to UO_2^{2+} . The other disproportionation product, U^{4+} , was oxidized back to UO_2^{2+} at 0.42 V vs. Ag/AgCl. These peak assignments are consistent with the conservation of charge within a complete scan cycle. These assignments were further confirmed by studying the relation between the peak height and the pH of the UO_2^{2+} solution by taking advantage of the proton-coupled electron transfer property of the UO_2^+ disproportionation reaction. In contrast to the

voltammograms of magnetite powder, one pair of peaks due to the redox reactions of $\text{UO}_2^{2+}/\text{UO}_2^+$ were found on the voltammogram of the bulk magnetite electrode. The cathodic and anodic charge density gradually approached similar values and a charge ratio of 1.2. The absence of a U^{4+} oxidation peak indicated the presence of stabilized UO_2^+ . The one-electron reduction of UO_2^{2+} on the bulk magnetite surface was further examined by the direct calculation of the number of electrons involved in the UO_2^{2+} reduction by fitting the potential step data to the Cottrell equation. The fast disproportionation of the UO_2^+ found on the surface of powder magnetite is tentatively attributed to the catalytic sites which can adsorb and desorb protons. Electrochemical methods provide an approach to identify the reduction product within minutes of the reaction occurring. The short time scale permits investigations of intermediate oxidation states, such as the metastable UO_2^+ species generated during the uranium reduction process. Ongoing experiments are focusing on the relation between the applied potential and the oxidation states of uranium deposited on the magnetite electrode using electrochemical-AFM, XPS, AES, and X-ray absorption spectroscopy.

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Appendix

A set of experiments was performed to test the reproducibility of the peak position and peak current of the cavity microelectrode, ideally only dependent on the type of sample but not the individual sample. This hypothesis was assessed by measuring the voltammograms of ferro/ferricyanide couple on magnetite + graphite for freshly prepared electrodes. A series of voltammograms (Fig SI1 and Fig SI2) were obtained in a solution containing 0.01 M ferrocyanide using the same microcavity electrode used for data collection in the manuscript. The electrode was packed with a magnetite + graphite mixture at a ratio of 10 wt.%.

Figure SI1 shows the CV data for a newly-packed electrode scanned for 20 cycles (bottom curve), and then the same electrode was continuously scanned for another three times and each time with 10 cycles (electrode was not removed from the solution). The first 20 cycles show a widening of the Fe(II)/Fe(III) peak separation as well as an increase in peak current. The peak position and height in the CV stabilizes after about 15-20 cycles.

In order to test the reproducibility over different samples, Figure SI2 overlays all experimental data for the 10 newly-prepared electrodes. During each run, the CV data were measured for the newly-prepared electrode for 20 cycles (left panel) and then the same electrodes were scanned for another 10 cycles to measure equilibrium conditions (right panel). Both peak separations and amplitudes on each newly-made electrode stabilized after 15-20 scans. One possible explanation for the increase of the Fe(II)/Fe(III) peak currents is that the packed electrode requires a brief “break-in” period before the electrochemical surface area is fully accessed by the solution. Another possible explanation could be due to progressive removal of passivation layers formed on the surface of the graphite and magnetite particles. Note diminishing reduction (negative) currents at potentials more negative than -0.4 V with increasing number of cycles.

From the voltammograms in Fig SI2, the peak values of the last scan in each experiment are listed in Table SI1 along with the calculated uncertainty in the measurement. The standard deviation of the peak current values is estimated to be $\pm 0.020 \mu\text{A}$. The peak separations are listed in Table SI2 with the calculated uncertainty of $\pm 5.5 \text{ mV}$.

In summary, this type of electrode shows reproducible data after a break-in period of 15-20 cycles.

Fig SI1. Reproducible test in ferrocyanide solution using magnetite + graphite electrode, the test was run on a freshly made electrode for 20 cycles and then run on the same electrode for 3 times and each time with 10 cycles.

Fig SI2. Reproducible test (10 runs) in ferrocyanide solution using magnetite + graphite electrode. Each test was run on a freshly made electrode for 20 cycles (left panel) and then run on the same electrode for another 10 cycles (right panel). The plot showed the overlay of all the 10 runs on the same graph. All the plots have the same current scales.

729 Table SI1. Peak current values from Fig SI2 and the standard deviation of the peak current
 730 values, all the peak current values are read from the last cycle in each run.

Freshly prepared electrode			Same electrode	
20 cycle run			10 cycle run	
electrode #	I _{pc} /μA	I _{pa} /μA	I _{pc} /μA	I _{pa} /μA
1	-0.640	0.675	-0.677	0.731
2	-0.618	0.650	-0.681	0.701
3	-0.657	0.676	-0.707	0.737
4	-0.600	0.629	-0.683	0.683
5	-0.609	0.672	-0.659	0.728
6	-0.600	0.637	-0.653	0.690
7	-0.625	0.653	-0.618	0.712
8	-0.616	0.644	-0.672	0.698
9	-0.622	0.625	-0.672	0.698
10	-0.642	0.681	-0.699	0.736
STD	0.0177	0.0196	0.0237	0.0191
Average STD		0.020 μA		

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733 Table SI2. Peak separations obtained from Fig SI2. The separations of the first cycle and the last
734 cycle were listed in each type of tests.

electrode #	Freshly prepared electrode		Same electrode	
	1 st cycle/mV	20 th cycle/mV	1 st cycle/mV	10 th cycle/mV
1	77.9	168.9	168.8	188.1
2	77.8	162.1	170.6	180.3
3	71.5	162.5	167.4	186.7
4	71.5	162.0	164.1	176.9
5	77.1	160.7	157.9	176.9
6	80.5	157.8	148.2	174.0
7	83.7	164.2	157.9	177.3
8	77.2	160.9	141.4	170.3
9	77.1	160.7	141.2	173.7
10	77.3	157.7	151.6	177.4
STD	3.4	3.0	10.4	5.3
Average STD		5.5 mV		

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Fig. 1. (a) Cyclic voltammograms of the empty cavity, magnetite powder, magnetite powder mixed with 10 wt.% graphite, and the SiO_2 powder mixed with 10 wt.% graphite using the cavity microelectrode (freshly-packed) in 0.01M ferrocyanide solution. Scan rate is 50 mV/s and repeated for 20 cycles. (b) Backscattered electron image of the magnetite powder mixed with 10 wt.% graphite. Light granular particles are magnetite and dark flakes are graphite.

Fig. 2. (a) Cyclic voltammograms of the newly-packed cavity microelectrode loaded with SiO_2 mixed with 10 wt.% graphite, empty cavity, magnetite powder and magnetite powder mixed with 10 wt.% graphite, respectively, in a 0.1 M Na_2SO_4 solution of pH = 3.4. (b) Voltammograms (measured on the same electrode) of the magnetite + graphite electrode scanned in 0.1 M Na_2SO_4 solution in a pH range from 3.44 to 5.19. The inserted voltammogram in (a) shows the square region of the peak A1, where the peak current increased as the Fe(II) concentration increased from 1.0 mM to 2.3 mM. Dashed arrows in (b) show the scan direction. The scan rate is 50 mV/s

and repeated from 15 cycles. The voltammograms of the last cycle in each measurement are showed above.

Fig. 3. (a) Cyclic voltammograms of the cavity microelectrode loaded with the mixed powder containing magnetite and 10 wt.% graphite in UO_2^{2+} solutions of concentrations from 1.2 mM to 4.2 mM. All the 10 cycles of voltammograms in each of the four solutions with different UO_2^{2+} concentration were showed, and different cycles in each concentration all overlapped with each other. (b) Linear relationship between the peak current and the UO_2^{2+} concentration. (c) Cathodic and anodic charge plot as a function of UO_2^{2+} concentration showed linear relationship and inserted graphs showed an example of charge integration in the 4.2 mM UO_2^{2+} solution. Peak current values (b) and integrated charges (c) were all referred to the voltammogram in 0.1M Na_2SO_4 as background current (Fig. 3.a, dashed line). The pH of the solution is 3.3 with the scan rate of 50 mV/s and 10 scan cycles each measurement. Error bars represent the standard deviation calculated from the data in 10 cycles. (d) Cyclic voltammograms of the cavity microelectrode loaded with SiO_2 mixed with 10 wt.% graphite, empty cavity, magnetite powder and magnetite powder mixed with 10 wt.% graphite, respectively, in a 4.2 mM UO_2^{2+} solution of pH = 3.3. The scans were repeated from 15 cycles on freshly-packed electrodes and only the voltammograms of the last cycle in each measurement are showed.

(a)

(b)

Fig. 4. (a) Cyclic voltammograms of uranyl redox reactions at different pH from 3.36 to 4.81 using a cavity microelectrode loaded with magnetite mixed with 10 wt.% graphite. Arrows point to the direction where pH was increasing. The UO_2^{2+} concentration is 2.3 mM, and the background solution is 0.1M Na_2SO_4 . The scan rate is 50 mV/s. (b) The concentration of aqueous uranium species changed as a function of pH, obtained by *Visual MINTEQ*. The dashed line represents the total amount of soluble uranium species in the solution.

(c)

(d)

Fig. 5. Cyclic voltammogram of uranyl redox reactions on the bulk magnetite electrode (a), and the dashed line in (a) is the voltammogram in a background solution containing 0.1M Na₂SO₄ of pH 3.5. The arrows in (a) point to the first scan cycle and grey regions highlight the integrated areas which were used to calculate the charge density of the last cycle. The cathodic and the anodic charge density changed as a function of the number of scan cycles (b). The inserted graph in (b) shows the charge ratio (ratio = cathodic charge / anodic charge) as a function of the scan cycle. The voltammogram of the bulk magnetite polarized at -0.6 V for 5 min before the cyclic voltammetric experiments (c). The solid line in (c) is the 1st cycle and the dashed line is the 2nd cycle. The diagram (d) shows the reduction of UO₂²⁺ to UO₂⁺ and subsequent disproportionation on the powder magnetite and the reduction of UO₂²⁺ to UO₂⁺ on the bulk magnetite. The pH of the UO₂²⁺ solution is 3.2 and the UO₂²⁺ concentration is 1.2 mM. The surface area of the electrode is 0.13 cm² and the scan rate is 50mV/s.

(a)

(b)

Fig. 6. Potential step chronoamperometry results of the bulk magnetite electrode in solution with and without UO_2^{2+} (a) and the current contribution from the UO_2^{2+} reduction obtained by subtracting the current in solutions without U(VI) from the current with U(VI) (a, inserted graph). Fitting of the number of electron transferred during the uranium reduction according to the Eq. (2) (b), where data points from 2 s to 10 s were used for fitting. The error bar represent the standard deviation from five separate measurements. The uranyl concentration is 1.2 mM with the background electrolyte of 0.1M Na_2SO_4 at pH=3.2, and the applied voltage is $-1.0\text{ V vs. Ag/AgCl}$.