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Redox potentials and kinetics of the Ce^{3+}/Ce^{4+} redox reaction and solubility of cerium sulfates in sulfuric acid solutions

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Abstract

Experimental work was performed with the aim of evaluating the Ce^{4+}/Ce^{3+} redox couple in sulfuric acid electrolyte for use in redox flow battery (RFB) technology. The solubility of cerium sulfates in 0.1–4.0 M sulfuric acid at 20–60 °C was studied. A synergistic effect of both sulfuric acid concentration and temperature on the solubility of cerous sulfate was observed. The solubility of cerous sulfate significantly decreased with rising concentration of sulfuric acid and rising temperature, while the solubility of ceric sulfate goes through a significant maximum at 40 °C. Redox potentials and the kinetics of the cerous/ceric redox reaction were also studied under the same temperature–concentration conditions. The redox potentials were measured using the combined redox electrode (Pt–Ag/AgCl) in equimolar Ce^{4+}/Ce^{3+} solutions (i.e.$[Ce^{3+}] = [Ce^{4+}]$) in sulfuric acid electrolyte. The Ce^{3+}/Ce^{4+} redox potentials significantly decrease (i.e. shift to more negative values) with rising sulfuric acid concentration; a small maximum is observed at 40 °C. Cyclic voltammetric experiments confirmed slow electrochemical kinetics of the Ce^{3+}/Ce^{4+} redox reaction on carbon glassy electrodes (CGEs) in sulfuric acid solutions. The observed dependencies of solubilities, the redox potentials and the kinetics of Ce^{3+}/Ce^{4+} redox reaction on sulfuric acid concentration are thought to be the result of inequivalent complexation of the two redox species by sulfate anions: the ceric ion is much more strongly bound to sulfate than is the cerous ion. The best temperature–concentration conditions for the RFB electrolytes appear to be 40 °C and 1 M sulfuric acid, where the relatively good solubility of both cerium species, the maximum of redox potentials, and the more or less satisfying stability of CGE s were found. Even so, the relatively low solubility of cerium salts in sulfuric acid media and slow redox kinetics of the Ce^{3+}/Ce^{4+} redox reaction at carbon indicate that the Ce^{3+}/Ce^{4+} may not be well suited for use in RFB technology. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

With increasing awareness of global warming and decreasing air quality, the shift away from traditional fossil fuels to renewable energy sources and the development of environmental friendly power sources such as batteries are of great importance [1]. Of all the new battery technologies currently under development around the world, the redox flow battery (RFB) appears to offer great promise as a low-cost, high-efficiency large-scale energy storage system for a wide range of applications [1–6].

Redox flow batteries are stationary storage batteries that operate by continually pumping two electrolytes past a pair of high-surface-area electrodes that are separated by an ionically conductive spacer. Energy is stored and harvested via the oxidation/reduction reactions of redox-active solutes in the two electrolytes. Redox flow batteries differ from conventional batteries because the active materials are concentrated solutions of redox-active solutes and not solid-state materials. This attribute offers several advantages compared with conventional batteries. The use of solutions to store the energy overcomes many of the loss-of-capacity problems associated with conventional batteries since dimensional changes in the active materials do not occur in the active materials. Liquid tanks allow for the separation of energy production and energy storage. So, a RFB can be harmlessly discharged, or stored at any state-of-charge for a long time with only negligible self-discharge or irreversible capacity loss. Using suitable inert electrode material and electrolyte solutions, solid-state electrochemical reactions are eliminated. The desired energy storage capacity can be set by the volume of the electrolytes in the tanks, and the power output of the system is determined by the size of the battery stack. Thus, RFB systems are easily

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scalable. The lifetime is extended, and the cost of maintenance is low [2–5].The most recent developments of RFB technology within the last decade are the Australian project "All Vanadium Redox Flow Battery" (AVRFB) [2–5] and the NASA and Japanese "Moon-Light" project [6]. In the latter one, the combination of Fe^{2+}/Fe^{3+} and Cr^{2+}/Cr^{3+} redox couples in hydrochloric electrolyte was investigated [6]. Emphasis on this research stalled because of the poor reversibility of the Cr half-cell and poor separation of electrolytes [7]. The AVRFB cell employs V^{3+}/V^{2+} and V^{5+}/V^{4+} redox couples in the negative and the positive half-cells, respectively. In 1997–1998, a 200 kW/800 kWh grid-connected vanadium battery was commissioned at the Kashima–Kita Electric Power Station in Japan, and after 150 charge–discharge cycles it was continuing to show high energy efficiencies of close to 80% at current densities of 80–100 mA/cm^2 [2–4]. Recent suggestions include the use of certain actinides, such as depleted neptunium that would otherwise be a long-lived radioactive waste, in RFB technology [7].

The active materials of the RFBs require two kinds of reversible redox couples, high solubility of the redox species in the electrolyte, and high potential difference between the two redox couples [2–5]. The specific energy of the cell is mainly determined by redox potential differences and concentration of species in the electrolyte. For optimization of the RFB constitution of the electrolyte, its concentration and the temperature influence on the redox species properties have to be considered.

The present experimental work was performed with the aim of evaluating the Ce^{3+}/Ce^{4+} redox couple in sulfuric acid electrolyte for use in a RFB. The Ce^{3+}/Ce^{4+} redox couple is attractive for RFB technology because of its very positive redox potential, which should result in a battery with a higher cell voltage and thus a greater energy storage capacity. For example, the vanadium RFB based on the V^{3+}/V^{2+} and V^{5+}/V^{4+} redox couples exhibits a cell voltage of approximately 1.3 V, whereas a similar cell based on the V^{3+}/V^{2+} and Ce^{3+}/Ce^{4+} redox couple is predicted to have a cell potential of 1.9 V, which is significantly larger.

The research consists of several parts: measurements of the electro-reaction rates in charge and discharge processes of cerium at carbon electrodes in sulfuric acid electrolyte, measurement of the electrochemical characteristics of Ce solutions, and measurement of the solubility of cerium sulfates in the sulfuric acid electrolyte. The purpose of this communication is to present the results of this research and evaluate the prospect using of the Ce^{3+}/Ce^{4+} redox couple in RFB technology.

2. Methods and procedures

2.1. Solubility

The determination of the solubility, or the concentration of the saturated solution, requires achieving the equilibrium between solution and solid state at a given temperature. The achievement of true equilibrium presents one of the biggest difficulties [5,8]; instead of several hours it can take many days of shaking at constant temperature.

Solid, anhydrous cerous sulfate $Ce_2(SO_4)_3$ of reagent analytical grade (Aldrich) was placed into the round bottom centrifuge vials of 50 ml volume capacity with screwed stoppers, and sulfuric acid of desired concentration (0.1, 1, 2, or 4 M) was added. The vials were placed in the shaking water bath (Precision Scientific) and shaken at constant temperature 20, 40, or 60 °C, with an accuracy of ±0.5 °C at 50 cycles/min. Cerous sulfate was added in the sufficient quantity so that excess solid was always present. Sampling and analysis were repeated several times during a 7–10 days period. The experiments indicated that the equilibration time for the $Ce_2(SO_4)_3$–H_2SO_4 system is about 10 days; however, shaking of the bottles was carried out continuously for at least 13–14 days.

Liquid samples were collected after keeping the solution for about 5 h without shaking so that the fine particles could settle completely. A membrane filter (Whatman, in syringe filter holder) with 0.45 μm pore size and the 10 ml plastic syringe were used to collect the liquid samples. The collected liquid samples were then analyzed for content of cerium.

From several dependable methods recommended in the literature [9,10], the direct complexometric titration [10] of cerium with disodium ethylenediaminetetraacetic acid (EDTA) and xylenol orange (XO) [9] indicator was chosen. The aliquot of saturated cerium solution was neutralized with NH_4OH (1:5) using acid–base indicator thymol blue, and then buffered with acetate buffer (pH 6). After adding of about 50 mg of dry mixture of 1% XO in KNO_3 the sample became red, and it was titrated with 0.02 M standard solution [11] of EDTA to an end point where the color of the solution turned from red to yellow. The validity and reproducibility of the method were checked by titration of known amount of the dry salt $Ce_2(SO_4)_3$, used in this experiment.

Solid ceric sulfate $Ce(SO_4)_2{\cdot}4H_2O$ of reagent analytical grade (Wako, Japan) was brought to the equilibrium with sulfuric acid in a similar way. Samples of saturated solutions were analyzed for content of cerium by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shimadzu 1000-III), to determine the equilibrium concentration of ceric ion in saturated solutions of ceric sulfate at given sulfuric acid concentration. Calibration curve was made using standard solutions of known Ce concentration and was checked prior to measurement to account for any drift in the instrument.

2.2. Redox potentials of the cerous/ceric ion couple

Four 0.05 M stock solutions of $Ce_2(SO_4)_3$ and four 0.1 M stock solutions of $Ce(SO_4)_2$ were prepared in 0.1, 1, 2 and 4 M sulfuric acid, and then they were mixed together in the 1:1 ratio with the purpose of preparing 0.05 equimolar

$c(Ce^{3+}) = c(Ce^{4+})$stock solutions with desired Ce and sulfuric acid concentration. The equimolar stock solution was then diluted with desired sulfuric acid solution to prepare 6–8 working solutions in the range 0.0008–0.05 M of both ions. Redox potential measurements were performed using the combined oxidation-reduction potential (ORP) electrode (model 91-79, Orion). This electrode consists of a Pt metal indicator electrode and a gel-filled Ag/AgCl reference electrode, both integrated into a single electrode body. Redox potentials, measured using this combined electrode, were converted to the standard hydrogen electrode scale by adding +224 mV, which is the value of the formal redox potential of the Ag/AgCl reference electrode, as indicated by the manufacturer. The ORP electrode was calibrated using the Orion redox standard solution after every set of solutions of the same sulfuric acid concentration.

A required amount of the solution was placed into the electrochemical cell (round-bottomed vials with screw caps). Samples were thermostated in the circulating water bath for at least 2 h to achieve equilibrium before measurements were acquired. To prevent diluting of solutions with the vapor from the hot water bath, vials were tightly closed. The combined redox electrode was placed into the rubber cap of suitable size to keep the sample closed also during measuring. Cells were refilled with fresh portions of equimolar solutions when temperature of bath was changed, and reported values are average of four samples of the same concentration.

2.3. Cyclic voltammetry of the cerous/ceric ion couple at glassy carbon

Studies of the redox kinetics of the Ce^{3+}/Ce^{4+} redox couple were pursued using cyclic voltammetry at a carbon glassy electrode (CGE). A 25 ml water-jacketed three-electrode cell, the glassy carbon working electrode, the platinum counter electrode, and the Ag/AgCl reference electrode were purchased from Bioanalytical Systems Inc. The special sealed cap, manufactured from PTFE, had entries for three electrodes, thin tubing for gaseous nitrogen purge and thermometer; the Orion ATC probe (automatic temperature control electrode) connected with Orion pH meter was used.

All cyclic voltammograms of 0.001–0.01 M solutions of cerous sulfate in 0.1–4.0 M sulfuric acid at 20, 40, and 60 °C were generated at scan rates between 0.02 and 0.5 V/s, using a CHInstruments model 660 electrochemical workstation. Prior to use, the CGE surface was polished to a mirror finish using the aqueous 0.3 mm and then 0.05 mm Al_2O_3 polishing suspension. Suspension particles were rinsed from the surface with water, then the electrodes were twice sonicated for 2 min in water to remove adherent alumina particles, then the electrodes were inspected visually under the microscope for presence of scars or adherent particles prior to use.

3. Results and discussion

3.1. Solubility

Literature data suggest that H_2SO_4 electrolyte in a wide range of concentration could be safely employed in continuous cycling, but the precipitation of cerium sulfates at higher sulfuric acid concentration, or even the hydrolysis of Ce^{4+} ion at lower sulfuric acid concentration can be expected. The possible precipitation of cerium species during the battery operation would depend on the solubility limits and induction times [5]; once precipitation began, it would continue until stability is achieved again. To predict supersaturation and precipitation of cerium species in sulfuric acid electrolyte, a systematic study of solubility of both ceric and cerous sulfates in sulfuric acid was undertaken to determine the optimal conditions of H_2SO_4 concentration and temperature where both of the cerium species are the most stable.

The saturation concentrations of cerous sulfate were determined at 20, 40, and 60 °C at sulfuric acid concentrations, which ranged from 0.1 to 4 M. Ceric sulfate solubility was studied at 0–6 M sulfuric acid. In both cases, the equilibrium sulfate concentrations were not analyzed. Results are listed in Table 1.

Table 1
Concentrations of cerium in saturated solutions of $Ce_2(SO_4)_3$ and $Ce(SO_4)_2$ at various concentrations of sulfuric acid and 20, 40 and 60 °C

H_2SO_4 (mol/l)	Ce^{3+} (10^3 mol/l)			Ce^{4+} (10^3 mol/l)		
	20 °C	40 °C	60 °C	20 °C	40 °C	60 °C
0	–	–	–	703 ± 8[a]	962 ± 10[a]	299 ± 10
0.1	298[a], 207 ± 15	122 ± 6	85 ± 5	757 ± 8[a]	910 ± 10[a]	238 ± 10
0.5	–	–	–	–	629 ± 7[a]	–
1	151 ± 6	97 ± 4	68 ± 4	426 ± 5	421 ± 5	232 ± 5
2	89 ± 3	80 ± 7	52 ± 5	276 ± 2	264 ± 2	277 ± 2
3	–	–	–	155 ± 2	154 ± 2	167 ± 2
4	20 ± 2	19 ± 2	15 ± 3	76 ± 2	76 ± 2	81 ± 2
6	–	–	–	25 ± 1	27 ± 1	32 ± 1

Average experimental values (±2 S.D.)
[a] Metastable values.

Considering the density of the sulfuric acid solutions, it can be concluded that our data on saturated molar concentration (mol/l) of cerous ion at 20 °C correspond well to the molal equilibrium concentration [12] of Ce^{3+} (mol/kg): 268 (0.05 M H_2SO_4); 176 (1.08 M H_2SO_4); 116 (2.16 M) and 26 (4.84 M H_2SO_4) at 25 °C. (Literature data [12], originally reported for $Ce_2(SO_4)_3$ in wt.% or mol/kg, are recalculated to mol/kg of Ce^{3+}).Equilibration of cerous ion in 0.1 M sulfuric acid was achieved quite slowly. The first sampling of $Ce_2(SO_4)_3$ solutions in 0.1 M H_2SO_4 after several days of shaking at 20 °C gave supersaturated values: big, colorless crystals were formed in the filtered sample after several days. Evidently the colloidal particles, which are too small to be removed by 0.45 μm filters, aggregated into larger particles over time. Sampling after 14 days of shaking gave stable results, while no supersaturation was observed at high sulfuric acid concentration (Fig. 1a.). Although the data for the ceric sulfate concentration in water and 0.1 M H_2SO_4 seem to represent a metastable state, because the filtered saturated solutions precipitated during 2–3 days, the solubility of $Ce(SO_4)_2$ decreases continuously with the rising sulfuric acid concentration (Fig. 1b.). The observed decreasing solubility of both ceric and cerous sulfates can be explained by the well known ''common ion effect'' i.e. increase of SO_4^{2-} ion concentration will lead to the decrease of the solubility of both cerium sulfates [13].

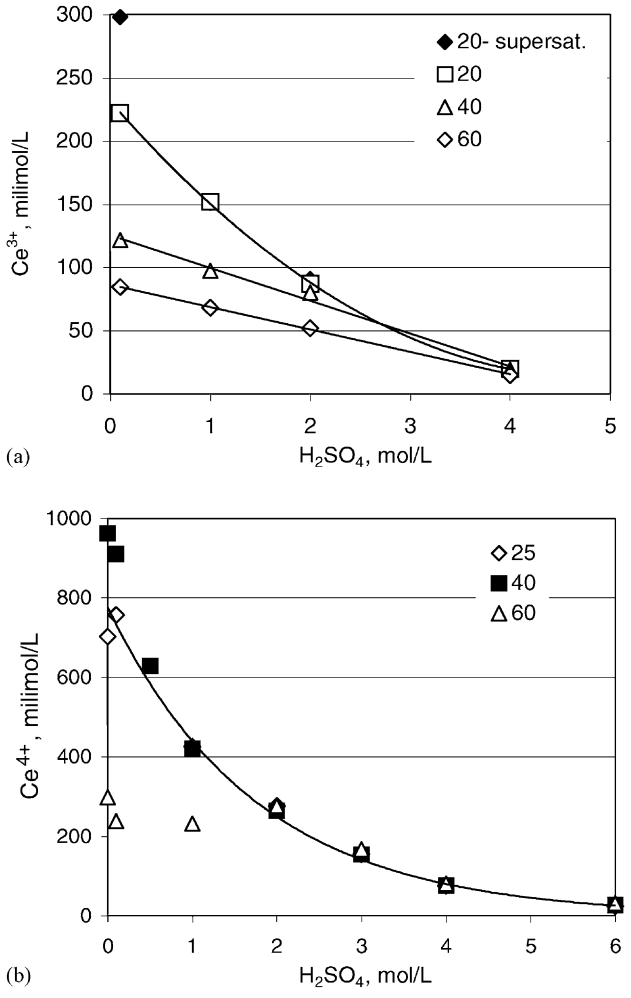

Fig. 1. Effect of temperature and sulfuric acid concentration on solubility of $Ce_2(SO_4)_3$ (a) and $Ce(SO_4)_2$ (b).

The effect of temperature on the solubility of both sulfates is most significant at sulfuric acid concentrations less than 2 M, and it is almost negligible in 4–6 M H_2SO_4. In many cases, dissolution of salts into aqueous solution is an endothermic process; therefore increasing temperature mostly increases solubility. However, the dissolutions of many lanthanide sulfates are reported to be exothermic reactions and rising temperature often results in a sharp decrease in their solubility [13,14]. That is what was observed for the solutions of $Ce_2(SO_4)_3$ considered in this study. Hence, the sulfate complexation of Ce^{3+} ion evidently has a negligible effect on solubility of cerous sulfate. On the other hand, the sulfato-complex formation, which is generally promoted by temperature and SO_4^{2-} concentration, would increase the solubility as it was observed in the sulfates of Sm^{3+} and Nd^{3+} [14]. Although neither in the case of Ce^{4+} the increasing sulfuric acid concentration resulted in increasing values of the solubility, the observed complex temperature dependence of the solubility with maximum at 40 °C can be explained by hydroxysulfate complexation reaction that resulted in a different reaction enthalpy of dissolution. This conclusion is supported by the fact that ceric ion hydrolyzes already at low concentration of acid [15–20]. Even in the case of a deficit of suitable complexing anion in the solvent, such as in perchloric acid solution (where no Ce^{4+} neither Ce^{3+} forms complexes), Ce^{4+} ion hydrolyzes to $[Ce(OH)]^{3+}$ which then dimerize [21,22] to $[CeOCe]^{6+}$.

The exothermic reaction of dissolving of $Ce(SO_4)_2$ in water and forming of metastable solutions, as well as metastable [19] $H_2Ce(SO_4)_3$ (orange) and $H_4Ce(SO_4)_4$ (English-red) in sulfuric acid were reported by Jones and Soper [19], who suggested that ceric sulfate exists either as the complex sulfatoceric acid ($H_4Ce(SO_4)_4$) or as the product of the hydrolysis of this acid, $H_4[CeO_x(SO_4)_{4-x}]$, and the solid tetrahydrate is then considered as $H_4[Ce(OH)_4(SO_4)_2]$ or the basic salt $H[Ce(OH)_3SO_4]$. Decreasing of the sulfuric acid concentration below 0.5 M is followed by the precipitation of basic sulfates [19], and the acid-basic titration confirmed that at this sulfuric acid concentration Ce^{4+} exists largely in the partially hydrolyzed state as $H_3Ce(OH)(SO_4)_3$; colorimetric measurements as the function of sulfuric acid concentration confirmed a progressing hydrolysis of Ce^{4+} with the decreasing concentration of sulfuric acid, with conversion to $H_2Ce(OH)_2(SO_4)_2$ and finally, to solid $HCe(OH)_3(SO_4)_3$ [19].

We also observed an unexpected precipitation of a pale yellow solid in 0.1 M sulfuric acid when 0.05 M $Ce_2(SO_4)_3$ and 0.1 M $Ce(SO_4)_2$ at 0.1 M H_2SO_4 were combined in volume ratio 1:1 with the aim to prepare the equimolar solution $c(Ce^{3+}) = c(Ce^{4+}) = 0.05$ M. The precipitate was

stepwise dissolved with additional portions of 0.1 molar sulfuric acid to a final equimolar concentration $c(Ce^{3+}) = c(Ce^{4+}) = 0.004$ M, where no precipitate was visually observed. The same 0.05 equimolar concentration in 1, 2 and 4 M sulfuric acid did not exhibit similar behavior.

The complex cerous-ceric sulfate as the cerous salt of sulfatoceric acid was regarded by Brauner [23], who wrote its formula as $CeH[Ce(SO_4)_4]\cdot 12H_2O$. Analogous complex sulfates can be prepared by replacing of cerous ion by trivalent ions of praseodymium, neodymium, and lanthanum. Twelve molecules of water [23] and observation by Jones and Soper [19] suggest that the formula of the observed pale yellow precipitate in 0.1 M sulfuric acid preferably might be either the complex cerous-ceric hydroxysulfate $Ce^{3+}[Ce^{4+}(OH)(SO_4)_3]$, or even basic ceric sulfate $H[Ce(OH)_3SO_4]$, which precipitated because the presence of Ce^{3+} disturbed its metastable equilibrium.

The observed solubility dependences are the complicated result due to the different solvation and complexation ability of Ce^{4+} and Ce^{3+} ions, as well as the different reaction enthalpy in dissolution and complexation; in addition, activity coefficients and ion strength also become very important parameters due to quite high Ce and H_2SO_4 concentration. Therefore, the solubility dependences on H_2SO_4 concentration and temperature need to be investigated further with the aid of quantitative investigation of the complex formation and their reaction enthalpies.

3.2. Redox potentials

Table 2 presents values of the formal Ce^{3+}/Ce^{4+} redox potentials, measured at 20, 40 and 60 °C in the four concentrations of sulfuric acid that were tested. We determined formal redox potentials of Ce^{3+}/Ce^{4+} redox reaction using combined platinum–Ag/AgCl electrode without a salt bridge; therefore, our values do not include some value of junction potential. They vary from the lowest value 1.422 V in 4 M sulfuric acid at 20 °C to 1.500 V in 0.1 M at 40 °C. The comparison of our values at 20 °C with literature data, mostly reported to 25 °C or room temperature [17,18,24,25] is good. For example, the Ce^{3+}/Ce^{4+} redox potential in 4 M sulfuric acid was reported as 1.42 V [24], and we found 1.422 V. Songina et al. [18] reported 1.45 V in 0.05 M H_2SO_4 at 25 °C, and we measured 1.46 V for in 1 M H_2SO_4 at 20 °C for the same cerium concentrations, so our and literature data are in a good agreement.

Reported formal Ce^{3+}/Ce^{4+} redox potentials were calculated using following equation:

$$E^0_{Ce^{3+}/Ce^{4+}} = E^0_{Ag/AgCl} + E_{comb,\,meas} \quad (1)$$

where, according to Nernst equation [11], measured potential $E^0_{comb,\,meas}$ in the case of equal molar concentration of redox species and constant temperature and pressure depends only on activity coefficients of cerium redox species:

$$E_{comb,\,meas} = E^0_{Ce^{3+}/Ce^{4+}} + \frac{RT}{F}\frac{\ln a_{Ce^{4+}}}{\ln a_{Ce^{3+}}} \quad (2)$$

Activity coefficients vary with ionic strength of solution; therefore, formal redox potential can be strongly affected by complexation of redox species or complexation with solvent.

Dependencies of the formal redox potentials on temperature and the cerous/ceric concentration in different sulfuric acid solutions are displayed in Fig. 2. No dependence on the cerium species concentration is observed in the range $c(Ce^{3+}) = c(Ce^{4+}) = 0.02$ M for all sulfuric acid concentrations and temperatures. A shift to more positive values of potential with increasing temperature was observed that suggests weaker complexation interactions of Ce^{4+} relative to Ce^{3+} at higher temperature. The influence of temperature rises with the concentration of sulfuric acid; the most significant dependence is in 4 M sulfuric acid. All potential

Table 2
Formal potentials Ce^{3+}/Ce^{4+} redox couple in sulfuric acid solutions

H_2SO_4 (mol/l)	Temperature (°C)	E^0 (±0.SS003 V)				
		0.002	0.004	0.008	0.02	0.04
0.1	20	1.473	1.474	1.476	Partially precipitates	
	40	1.496	1.500	1.497		
	60	1.477	1.484	Precipitates		
1	20	1.454	1.457	1.462	1.465	1.466
	40	1.479	1.484	1.486	1.488	1.489
	60	1.463	1.468	1.474	1.482	1.485
2	20	1.443	1.450	1.453	1.454	1.454
	40	1.457	1.470	1.478	1.480	1.480
	60	1.451	1.468	1.475	1.482	1.484
4	20	1.422	1.427	1.429	1.431	1.431
	40	1.431	1.448	1.455	1.459	1.460
	60	1.451	1.466	1.474	1.479	1.480

$c(Ce^{3+}) = c(Ce^{4+})$ mol/l.

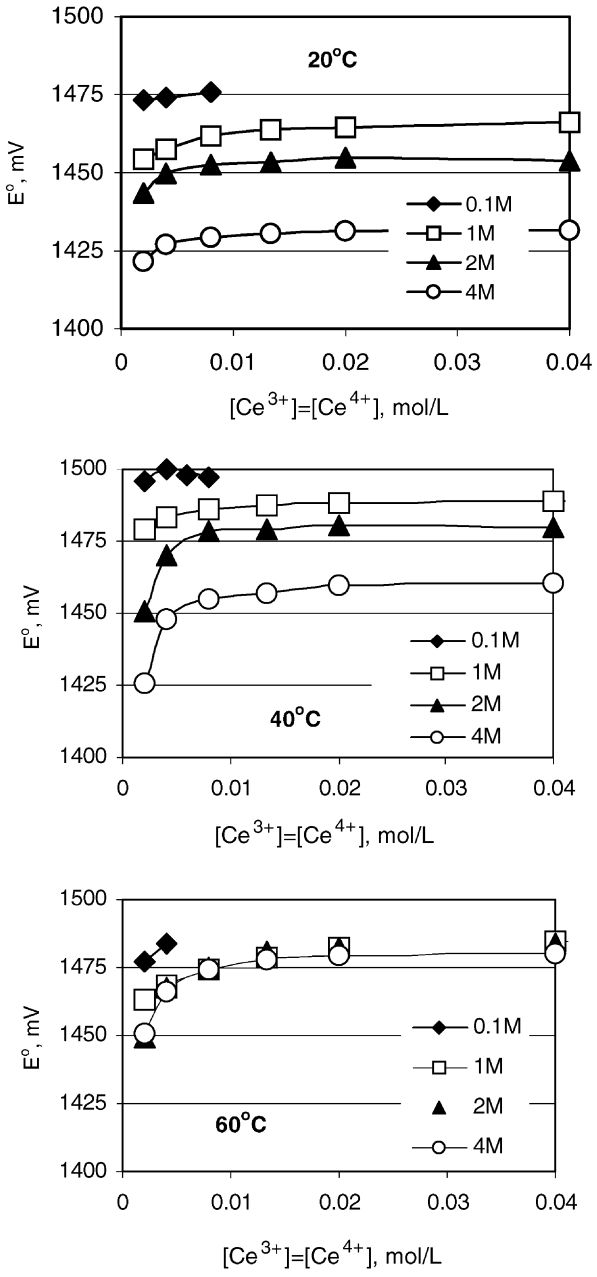

Fig. 2. Effect of cerium species concentration on formal redox potential at 20–60 °C.

values in 1 M sulfuric acid are the highest at 40 °C, and at 60 °C all three 1, 2 and 4 M sulfuric acid dependencies go as one line. The maximum of redox potentials at 40 °C at 0.1 and 1 M sulfuric acid corresponds with the temperature dependence of the ceric ion solubility at low sulfuric acid concentrations.

The shift to less positive potentials with increasing concentration of H_2SO_4 is a result of the formation of sulfate complexes of the tetravalent ceric ion [15,16,18–22,26]. Values of the stepwise stability constants of Ce^{4+} to $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_3^{2-}$, equal to 3500, 200 and 20, respectively, were reported by Hardwick and Robertson [21,22], who studied electromigration and absorption spectra of solutions of ceric sulfate in sulfuric acid. The activity of the free ceric Ce^{4+} is considerably lower than its formal concentration, because as mentioned Wadsworth et al.[26], practically all the tetravalent cerium is complexed and present as $Ce(SO_4)_3^{2-}$, and in the case of Ce^{3+} ions approximately half are in the complexed form, i.e. $[Ce^{3+}(SO_4)]^+$. Additionally, in diluted solutions not only sulfate complexation, but also the hydrolysis of Ce^{4+} takes place [15–18], and can lead to a decrease in the redox potential of the system that was confirmed by spectrophotometric studies of 10^{-4} M solutions of the tetravalent cerium [18]. Although the concentrations of Ce^{3+} and Ce^{4+} started out the same, it is evident that the activities of the reduced and oxidized cerium species are not always equal each other in the real system. Therefore, the different complex formation ability of Ce^{4+} and Ce^{3+}, as well as the decrease of solubility (with change of the temperature and the electrolyte concentration) bring changes in the redox species activities and result in a complicated temperature dependence of redox potential.

3.3. Kinetics of Ce^{3+}/Ce^{4+} electrochemical processes on carbon glassy electrodes

The electrochemical kinetics of the Ce^{3+}/Ce^{4+} redox couple on different electrodes have been studied by different authors [15–18,20,27–29] at room temperature. Carbon electrodes are of technological importance and are widely employed in RFB technology; therefore, their use was the subject of our interest. In this work the cyclic voltammetry with a GCE was performed at 20, 40 and 60 °C with solutions of 0.006–0.01 M $Ce_2(SO_4)_3$ in 0.1, 1, 2 and 4 M sulfuric acid electrolyte. Cyclic voltammograms of reversible one-electron processes [30] are expected to exhibit anodic and cathodic peak potential separations $\Delta E_p = 58$ mV (at 25 °C), equal anodic and cathodic peak currents, and the quotient of the peak current (i_p) and the square-root of the scan rate ($v^{1/2}$) is a constant value, independent of v. The electrochemical process is considered reversible if the electron transfer kinetics are fast on the experimental time scale. Hence, if the standard heterogeneous electron transfer rate constant is sufficiently small, the process is quasi-reversible, characterized by a peak potential separation $\Delta E_p > 58$ mV, which increases with increasing v [31].

Comparing the obtained voltammograms for Ce^{3+} oxidation in Fig. 3 with the expectations of theory [32], it is clear that the studied redox process is quite slow, i.e. it exhibits low reversibility. The peak splittings in Fig. 1a are all quite large, i.e. 400 mV in 4 M H_2SO_4 to almost 1200 mV in 1 M H_2SO_4 at 20 °C. The large peak splittings indicate a very slow interfacial electron transfer process. Peak splittings were found to increase with increasing scan rate, which is strongly consistent with them being caused by slow interfacial electron transfer. The observation of particularly large peak splittings at the lowest sulfuric acid concentration

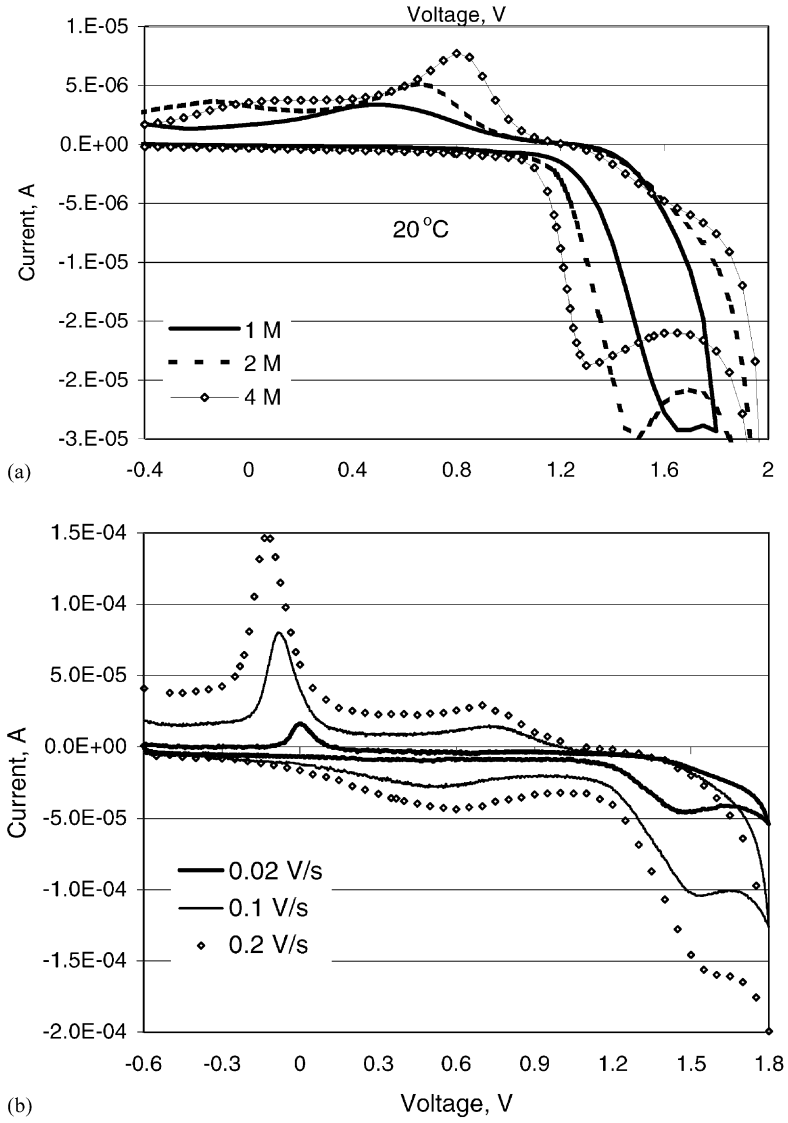

Fig. 3. (a) Cyclic voltammogram of 6 mmol/l of Ce^{3+} in 1, 2, and 4 M H_2SO_4 at the scan rate 0.02 V/s and 20 °C; (b) cyclic voltammogram of $Ce_2(SO_4)_3$ (6 mM Ce^{3+}) at 2 M H_2SO_4 and 40 °C.

studied suggests that the $Ce^{3+/4+}$ redox reaction is especially slow under these conditions. This observation could be explained by an especially large structural change associated with a conversion between Ce^{3+} and Ce^{4+} under these conditions. We note that a similar structural change was postulated to explain the observed shifts in redox potential with changing sulfuric acid concentration noted in Section 3.2. The effects of Ce^{3+} concentration on the electron-transfer rates appear to be minimal (data not shown).

We also observed that the electrode experimental behavior can depend by unpredictable way on the electrode surface pre-treatment and history of the CGE. Also, the first scan in the series of voltammograms was often different from the subsequent scans. This behavior makes it difficult to make a quantitative analysis of the results. Even so, the fact that the behavior depends so strongly on the electrode pre-treatment does provide some information about the role of the carbon surface structure in promoting the Ce^{3+}/Ce^{4+} electron transfer.

One significant effect of increasing the temperature and the sulfuric acid concentration is that it leads to a degradation of the GCE surface, probably via chemical oxidation. This effect is already seen at 2 M H_2SO_4 and 40 °C (Fig. 3b), in the form of unexpected reductive peaks near 0.0 V that are believed to be associated with irreversible carbon surface oxidation. As it was reported in the literature [33], a substantial surface modification of carbon electrodes following electrooxidation in sulfuric acid media might be enhanced at high temperatures and high sulfuric acid concentrations. Two of three CGE were visibly damaged after the voltammetry in 4 M H_2SO_4 at 40 °C or 2 M H_2SO_4 at 60 °C. There was a visual evidence of the blister formation on the surface under conditions of hot and more concentrated sulfuric acid. This ‘‘pitting’’ in the electrode surface did not disappear

after polishing. The voltammetry of these electrodes often lacked the return peak for Ce^{4+} reduction, which suggests that the Ce^{4+} is consumed in a follow-up chemical reaction, possibly also involving carbon oxidation. Surprisingly, the third electrode, however used under the same experimental conditions, exhibited almost no damages after the intensive polishing.

Further work would be required to sort out all of the details of this chemistry, but even without such a detailed study it seems clear that the combination of carbon and hot concentrated sulfuric acid could be a problem and possibly should be avoided in a practical RFB device.

4. Summary

The solubility of ceric and cerous sulfates, the redox potentials of the Ce^{3+}/Ce^{4+} redox ion couple, and the electrochemical kinetics of the Ce^{3+}/Ce^{4+} redox reaction were studied at 20, 40, and 60 °C in 0.1–4 M sulfuric acid. A synergistic effect both of the sulfuric acid concentration and the temperature on the solubility of the cerous and ceric sulfates was significant; in both cases the process of dissolving was found to be exothermic and the rising temperature resulted in a sharp decrease in their solubility. Increasing sulfuric acid concentration caused the "common ion effect" hence decreased the solubility of cerium sulfates. However, in both cases of Ce^{3+} and Ce^{4+}, the complexes formation showed negligible effect on their solubilities. Changes of the Ce^{3+}/Ce^{4+} redox potential values with increasing sulfuric acid concentration and decreasing temperature and the slow electrochemical kinetics of Ce^{3+}/Ce^{4+} redox reaction on GCE in sulfuric acid solutions are thought to be the result of non-equal complexation of both redox species, cerous and ceric ions, by sulfate anions into anionic sulfate complexes. It could be concluded that 40 °C should be the best temperature condition in the RFB electrolytes with 1–2 M sulfuric acid electrolyte; however, the carbon electrode surface was damaged at higher temperature and increased sulfuric acid concentration, which may affect the RFB operation.

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