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Electrochemical Oxidation and Speciation of Lanthanides in Potassium Carbonate Solution

Poki Tse,[1,2] Nathan P. Bessen,[2] Shane S. Galley,[1] Samuel A. Bryan,[1] Amanda M. Lines,[1,z] and Jenifer Shafer[2,z]

[1] *Pacific Northwest National Laboratory, Richland, Washington 99354, United States of America*
[2] *Department of Chemistry, Colorado School of Mines, Golden, Colorado 80401, United States of America*

Increasing lanthanide demand to support clean energy goals drives the need to develop more efficient approaches to separate adjacent lanthanides. Most approaches for lanthanide separations are not very selective and are based on small differences in lanthanide ionic radii. Concentrated potassium carbonate media has shown some potential to enable oxidation of praseodymium (Pr) and terbium (Tb) to their tetravalent states, which could ultimately enable a separation based on differences in oxidation states, but very little is known regarding the system's chemistry. This work completes a detailed examination of cerium (Ce) redox chemistry in concentrated carbonate media to support the development of Pr and Tb oxidation studies. The half-wave potential ($E_{1/2}$) of the Ce(III)/(IV) redox couple is evaluated under various solution conditions and computational modeling of carbonate coordination environments is discussed. Cyclic voltammetry shows higher carbonate concentrations and temperatures can lower the potential required to oxidize Ce(III) by 54 mV (3.5 to 5.5 M) and 39 mV (from 10 °C to 70 °C). Chronoabsorptometry shows Ce(III) and Ce(IV) carbonate complexes are chemically stable and reversible. Computational modelling suggests the most likely coordination environment for the Ce(IV) complex is $Ce(CO_3)_4(OH)^{5-}$ which is less entropically favorable than the lowest energy Ce(III) complex, $Ce(CO_3)_4{}^{5-}$.

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Lanthanide demand has been increasing due to various applications in the industrial and clean energy sectors, but the large amounts of acid and organic solvent used during mineral dissolution and purification associated with mining and preparation of lanthanide ores causes serious environmental impacts.[1] Interest exists in minimizing the environmental impact of lanthanide purification by improving the efficiency and selectivity of lanthanide separations. Lanthanide separation efficiency is largely hindered by separating lanthanides from each other (i.e. intragroup separations). The lanthanides share very similar chemistry within the group because the f-orbital electrons are buried within the electron core of a given lanthanide atom, which causes them to have similar ionic radii and oxidation states. This makes development of effective lanthanide separations schemes a grand scientific challenge.[2–4] A separation method based on more profound chemical differences between the lanthanides than slight differences in ionic radii is preferred.

Intragroup lanthanide separations are currently achieved by using chromatography with aqueous-based complexants or multistage solvent extraction.[1] Chromatography is an approach with limited throughput and solvent extraction generates large volumes of hazardous waste. The associated hazardous waste generated through use of these techniques, especially solvent extraction, on a large scale limits their long-term viability due to the environmental impact of the technology. A different approach for lanthanide separation based on alternating the oxidation state of redox active lanthanides could potentially yield significantly improved separations.[5,6] This has been well demonstrated for americium/curium separations, where separation factors between americium and other trivalent f-elements can increase by >1000x by oxidizing the americium to the hexavalent state.[7–11]

Neodymium (Nd), dysprosium (Dy), and terbium (Tb), which have significant importance in clean energy development, have been determined critical for intragroup lanthanide separation (praseodymium (Pr) from Nd and Tb from Dy).[12] Fortunately, Pr and Tb have potentially accessible tetravalent oxidation states to encourage a separation based on a less common oxidaion state. The major challenge of completing separations based on oxidation of relevant lanthanides is to lower the potential required to oxidize certain lanthanides (including Pr and Tb) within the potential range at which water is stable. Several studies have demonstrated the electrochemical oxidation of Ce in acidic media.[13,14] In particular, the required electrode potential to oxidize cerium (Ce(III)) is +1.5 V (vs Ag/AgCl) in 1 M perchloric acid ($HClO_4$),[15,16] while the electrode potential for Pr(III) and Tb(III) is +3 V (vs Ag/AgCl) and +2.9 V (vs Ag/AgCl), respectively.[15,16] This is well outside the stable potential range for water which is around 1.0 V (vs Ag/AgCl) at around pH 0.[15–17] This high required potential significantly impacts data collection and analysis in aqueous media.

In an effort to bring these potentials into an aqueous system that could be studied, Hobart et al. showed that select lanthanides, Ce (III), Pr(III) and Tb(III), could be oxidized to the tetravalent state in concentrated carbonate ($CO_3{}^{2-}$) media.[18] The potential required to oxidize Ce(III) is −0.15 V (vs Ag/AgCl) in concentrated carbonate media. This 1.65 V stabilization in carbonate media was attributed to the stronger complexation of the tetravalent lanthanides by $CO_3{}^{2-}$ over $ClO_4{}^{-}$ ions. They also oxidized Pr(III) and Tb(III) in carbonate media with potentials +1.2 V (vs Ag/AgCl) and +1.1 V (vs Ag/AgCl), respectively, bringing these potentials closer to the water stability window which is around +0.3 V (vs Ag/AgCl) at around pH 13.[17] Several works have explored the effect of solution conditions on the stability of Tb(IV) complex in basic media.[19–22] Varlashkin et al.[19] completed preliminary work on the influence of solution conditions on lanthanide oxidation where they found higher $CO_3{}^{2-}$ concentration can increase the solubility of chemically oxidized Tb(IV). Studies of Ce(IV) in lower $CO_3{}^{2-}$ concentration media (around 1 M) suggest the stoichiometry for the Ce(IV) limiting complex is $Ce(CO_3)_6{}^{8-}$.[23,24] To date, there is no complete study on the effect of solution conditions on the half-wave potential ($E_{1/2}$) of Ce(IV), Pr(IV) and Tb(IV) complexes and no suggested coordination environment of the Ce(IV) complex in concentrated carbonate media (i.e. $\geqslant$5.5 M).

Understanding how solution conditions impact the Ce(III)/Ce (IV) redox couple can help inform how to further lower the potential required for Pr and Tb oxidation in concentrated carbonate media. This work studied the impact of changing $CO_3{}^{2-}$, Ce(III), and hydroxide (OH^-) concentrations, and temperature on $E_{1/2}$. Many electrochemical attempts were used to drive Pr and Tb oxidation in this media, both as a part of this study and other reports, but none showed quantitative, electrochemical evidence for the presence of Pr

[z] E-mail: amanda.lines@pnnl.gov; jshafer@mines.edu

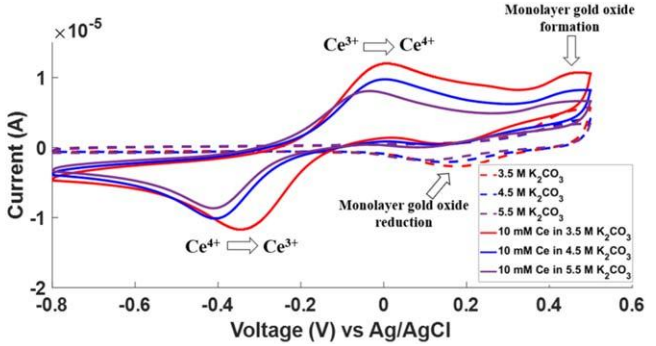

Figure 1. The cyclic voltammogram of 10 mM Ce at 3.5 (red solid line), 4.5 (blue solid line) and 5.5 M (purple solid line) K_2CO_3 concentrations and the corresponding K_2CO_3 cyclic voltammogram. The anodic peak around 400 mV and the cathodic peak around 200 mV is the monolayer gold oxide formation peak and reduction peak in the basic media respectively.[39]

(IV) and Tb(IV).[18,19] While Tb solutions did turn yellow when +1.4 V (vs Ag/AgCl) was applied to mixed 5.5 M K_2CO_3 and 1 M KOH solution, no quantitative UV–vis spectra could be collected due to water oxidation creating bubbles of oxygen in the cuvette. Utilizing ozone produced a color change of Tb and Pr and the collected UV–vis spectra was similar to the literature.[18] Several studies have examined the structure of Tb(IV) and Pr(IV) complexes.[25–27] The coordination environment of the Ce(III) and Ce(IV) complexes in concentrated carbonate media were considered using computational studies to understand why oxidation is promoted in CO_3^{2-}. This work will be beneficial for future development of redox-based lanthanide separations.

Experimental

Chemicals and materials.—Cerium (Ce^{3+}) and terbium (Tb^{3+}) hydrated chloride salts ($CeCl_3{\cdot}7H_2O$, 99.999% purity; $TbCl_3{\cdot}6H_2O$, 99.999% purity) and anhydrous praseodymium chloride salt ($PrCl_3$, 99.99% purity) were procured from Sigma-Aldrich as reagent-grade salts, used as received, and stored in a desiccator. Potassium hydroxide (KOH, 90% purity), terbium nitrate ($Tb(NO_3)_3{\cdot}5H_2O$, 99.9% purity) and silver nitrate ($AgNO_3$, 99.0% purity) were purchased from Sigma-Aldrich as reagent-grade salts and used as received. Due to the lower purity of the KOH, solutions of KOH were titrated to confirm the 90% purity and that the impurities did not contribute to any unexpected acid or base chemistry. Ammonium persulfate ($(NH_4)_2S_2O_8$, 98% purity) was purchased from Acros Organics as reagent-grade salts and used as received. Sodium bismuthate ($NaBiO_3$, 95% purity) was purchased from J.T. Baker as reagent-grade salts and used as received. Hydrated terbium chloride was utilized in both electrochemical and chronoabsorptometry experiments with UV–vis spectroscopy while terbium nitrate was only utilized in chronoabsorptometry experiments with Raman spectroscopy. Potassium carbonate (K_2CO_3, 99% purity) was obtained from Sigma-Aldrich as a reagent-grade salt, dried in an oven for 1 h at 270 °C,[28] and stored in a desiccator before use. The carbonate solutions were prepared by dissolving an appropriate amount of the carbonate salt in $\geqslant 18$ MΩ cm deionized water (with total organic carbon less than 10 ppb). The lanthanide solutions were prepared by dissolving an appropriate amount of lanthanide solids in the carbonate solution.

Instrumentation.—The electrochemical setup used a BASi Epsilon potentiostat in conjunction with an Au disk working electrode, which was purchased from BASi, a Pt auxiliary electrode, and an Ag/AgCl, 3.5 M KCl reference electrode. The Au disk electrode was cleaned and polished prior to use utilizing a BASi polishing kit with polishing pads and alumina polish. All potential measurements were made vs Ag/AgCl in 3.5 M KCl and reported as Ag/AgCl in 3.5 M KCl unless otherwise indicated. All cyclic voltammetry experiments were run for four cycles and the data of third cycle was utilized unless otherwise indicated. The temperature control for the temperature variation experiments was provided by a Cole-Parmer Polystat Recirculator. The recirculator was set between 10 °C–70 °C and the temperature of the water bath throughout the experiment was within ± 1 °C of the intended temperature.

Two spectroelectrochemical (SEC) setups were used. Setup #1 was used to collect the Pr and Tb experimental data while setup #2 was used to collect the Ce experimental data. Setup #1 combined the BASi Epsilon potentiostat with an Ocean Optics DH-MINI deuterium tungsten halogen light source and a Flame spectrometer (OceanView software). Rectangular Au mesh electrodes were cut from larger sheets of mesh and were attached to Au wire, via weaving the wire through the mesh (both wire and mesh were purchased from Fisher Scientific). The Pt auxiliary electrode and Ag/AgCl, 3.5 M KCl reference electrode were used. Specialized SEC cells with a 1 mm path length quartz cell purchased from BASi was used. Setup #2 combined a Pine Wavenow potentiostat (Aftermath software) and Avantes AvaSpec-ULS2048 spectrometer. The Au honeycomb working and counter electrode were obtained from the Pine honeycomb electrode kit. The reference electrode was an Ag wire, coated with solid AgCl, immersed in a KCl gel electrolyte which was included in the Pine honeycomb kit. Specialized Pine SEC cells with a 1.7 mm path length quartz cell were used.

Computational details.—Computational modelling was done using similar conditions to those used by Bessen et al.[29] The structures of the complexes were optimized using density functional theory (DFT) with a PBE functional, a scalar-relativistic zeroth-order regular approximation Hamiltonian,[30–32] and a triple-ξ plus one polarization function basis set with a small frozen-core approximation[33] in ADF 2019.104.[34] Frequency calculations were used to confirm the structures which were optimized to a minimum and to calculate entropy. After optimization of the structures, single-point energy calculations of the complexes were completed using the aforementioned conditions with a PBE0 functional and no frozen core for further validation. In addition to any explicitly defined water molecules, solvation by water was implicitly applied by the COSMO solvation model where atomic radii were set to the Allinger radii divided by 1.2.[35]

Result and Discussion

Cerium (Ce).—The only reported lanthanide that was electrochemically oxidized to the tetravalent state prior to 1980 is Ce.[19] This is because the required potential to oxidize the other trivalent lanthanides is much higher than the stability region of water. The focus of the following sections is to evaluate the effect of various solution conditions including carbonate concentration, lanthanide concentration, hydroxide concentration and temperature on the half-wave potential ($E_{1/2}$) of the Ce(III)/Ce(IV) couple. In addition, the stability and coordination environment of Ce(III) and (IV) will also be examined via chronoabsorptometry and computational study.

K_2CO_3 concentration.—The work completed by Hobart et al.[18] showed the required potential to oxidize Ce(III) is 1.65 V lower in 5.5 M CO_3^{2-} media compared to 1 M $HClO_4$ media. In that study Hobart proposed the low electrode potential is due to the complexing feature of CO_3^{2-}, which helps stabilize Ce(IV).[18] The downward shift of the electrode potential in CO_3^{2-} complexing media indicated the resultant product is more stable than with the non-complexing ion.[36,37] This hypothesis was further evaluated in this study by varying the CO_3^{2-} concentrations from 3.5 M to 5.5 M at room temperature to examine the relationship between the half-wave potential ($E_{1/2}$) and the CO_3^{2-} concentration. The representative cyclic voltammograms (CV) of 10 mM Ce(III) in various CO_3^{2-} concentrations, at a scan rate of 100 mV s^{-1}, are shown in Fig. 1. As shown in Fig. 1, $E_{1/2}$ decreased with CO_3^{2-} concentration where the $E_{1/2}$ of 10 mM Ce in 3.5, 4.5 and 5.5 M K_2CO_3 is −169.5, −199 and

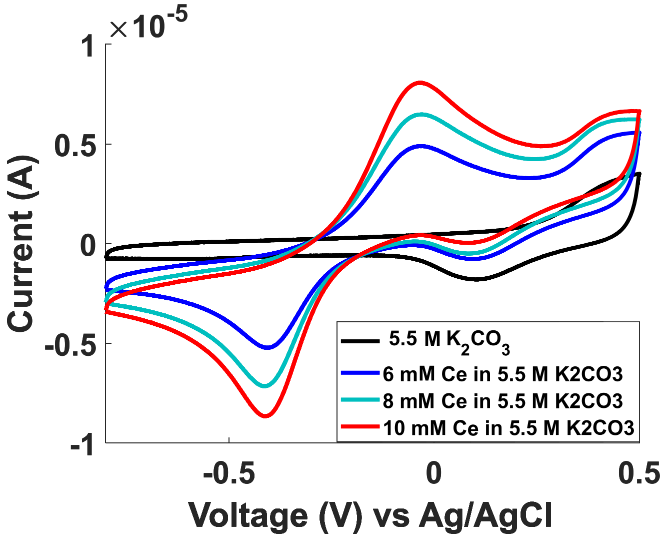

Figure 2. The cyclic voltammogram of various [Ce] in 5.5 M K_2CO_3 at 100 mV s^{-1}. The $E_{1/2}$ of 6 mM, 8 mM and 10 mM [Ce] in 5.5 M K_2CO_3 is −218 mV, −223.5 and −223.5 mV respectively.

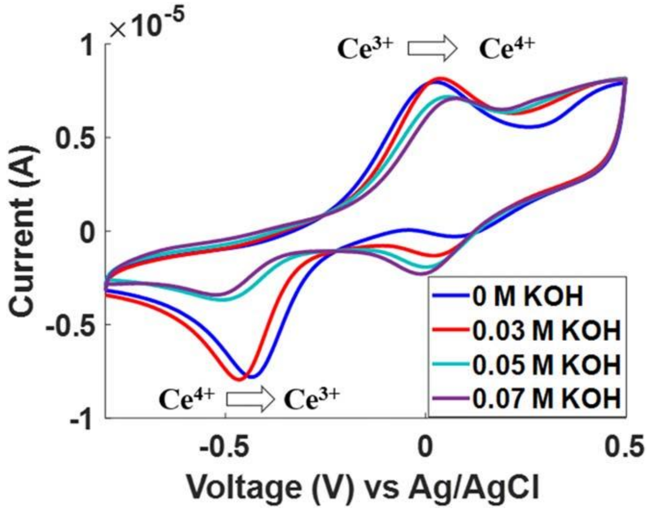

Figure 3. The cyclic voltammogram of 10 mM Ce in 5.5 M K_2CO_3 in various [KOH] at 100 mV s^{-1}.

Table I. The electrochemical data of 10 mM Ce in 5.5 M K_2CO_3 with various KOH concentrations.

[KOH]	$E_{1/2}$ (mV)	Δ E (mV)
0 M	−207.5	449
0.03 M	−214.5	499
0.05 M	−228.5	565
0.07 M	−229.5	601

−223.5 mV, respectively. This can be interpreted as the Ce(IV) carbonate complex being stabilized by the higher concentration of coordinating CO_3^{2-} ions. The resultant Δ E of Ce(IV) reduction and Ce(III) oxidation in various CO_3^{2-} concentrations is larger than predicted for a one-electron, electrochemically reversible system which is 59 mV[38] indicating this is an electrochemically quasi-reversible system.

A non-Nerstian approach was used to estimate the diffusion coefficient of Ce(III) and Ce(IV) in concentrated CO_3^{2-} media, Eqs. 1 and 2,[40,41]

$$i_p = 2.99 \times 10^5 \alpha^{1/2} n^{3/2} A C D^{1/2} \nu^{1/2} \quad [1]$$

$$|E_p - E_{p/2}| = \frac{1.857\, RT}{\alpha n F} \quad [2]$$

where i_p represents the anodic or cathodic peak current, α represent the transfer coefficient, n represents the number of electrons transferred in the redox reaction, A represents the electrode surface area, which is 0.0201 cm^2. D represents the diffusion coefficient of the analyte, C is the bulk concentration of analyte, E_p represents the oxidation or reduction peak voltage, $E_{p/2}$ is the half-peak potential, R represents the gas constant, T represents temperature, and F represents the Faraday's constant. The peak current was determined from extrapolation of the baseline current according to the method of Kissinger and Heineman.[38] The measured diffusion coefficient of Ce(III) and Ce (IV) in 5.5 M K_2CO_3 is 2.35×10^{-7} and 8.37×10^{-8} cm^2s^{-1}, respectively. The diffusion coefficient of Ce(IV) reported in approximately 1 M Na_2CO_3 is 1.14×10^{-6} cm^2s^{-1}.[23] This discrepancy could be attributed to the possible formation of a monolayer on the electrode surface, a different concentration of the background electrolyte, or the use of different electrode materials which will have different propensities for the electron transfer between analytes and electrode materials and so affect the diffusion coefficient.[23] Figure S.1 (available online at stacks.iop.org/JES/169/046521/mmedia) shows a linear relationship between (i_p) and the square root of scan rate ($\nu^{1/2}$) and concentration of Ce (M) which indicates both Ce(III) and Ce(IV) are freely diffusing redox species.[42] The slight deviation from a line with a y-intercept of zero, as would be expected by theory, is likely due to the Ce(III)/(IV) couple being quasi-reversible.

Ce(III) concentration.—The next factor examined in this work is the impact of lanthanide concentration on the half-wave potential ($E_{1/2}$) of Ce at constant CO_3^{2-} concentration. The Ce(III) concentration was varied from 6 mM to 10 mM in 5.5 M K_2CO_3, Fig. 2. The diffusion coefficients of Ce(III) and Ce(IV) in 5.5 M K_2CO_3 were also calculated while varying the Ce concentration, resulting in diffusion values of 2.31×10^{-7} and 8.88×10^{-8} cm^2s^{-1}, respectively. These values are in good agreement with the diffusion coefficients calculated from K_2CO_3 variation studies, *vide supra*, from varying scan rates, Fig. S.1. As seen in Fig. 2, varying the Ce (III) concentration does not change the $E_{1/2}$, which has been reported by other studies at a lower CO_3^{2-} concentration of 1 M.[24,43] This result also indicates Ce(III) in carbonate media is a mononuclear complex as the $E_{1/2}$ is independent from the concentration of Ce(III).[24] If the Ce carbonate complex is a polynuclear complex, the $E_{1/2}$ would be expected to change with the Ce concentration.[24,43]

OH^- concentration.—The study by Hobart et al.[18] suggested the stability of Tb(IV) and Pr(IV) complexes in CO_3^{2-} media can be increased by adjusting the concentration of OH^- to approximately 1 M. To study this more, the effects of the concentration of KOH on the $E_{1/2}$ of Ce was examined. The studies were limited to a maximum concentration of 0.07 M KOH because a white colloid was observed at higher concentrations concurrent with a decrease in the peak height. This solid appeared stable overnight. Figure 3 shows the cyclic voltammograms for 10 mM Ce(III) in 5.5 M K_2CO_3 as a function of increasing KOH concentration. The peak height of both the anodic and cathodic peak of Ce decreases with increasing KOH concentration presumably due to the formation of insoluble solid Ce hydroxide complexes.

Both the anodic and cathodic peak height of Ce decreased with the number of scans, so the data from the second cycle is shown for a more distinguishable peak than the third cycle would give, Fig. S.2. This observation might indicate an electrochemical-chemical (EC) mechanism where electrochemically oxidized Ce(IV) might react with OH^- to potentially form a relatively stable, heteroleptic cerium

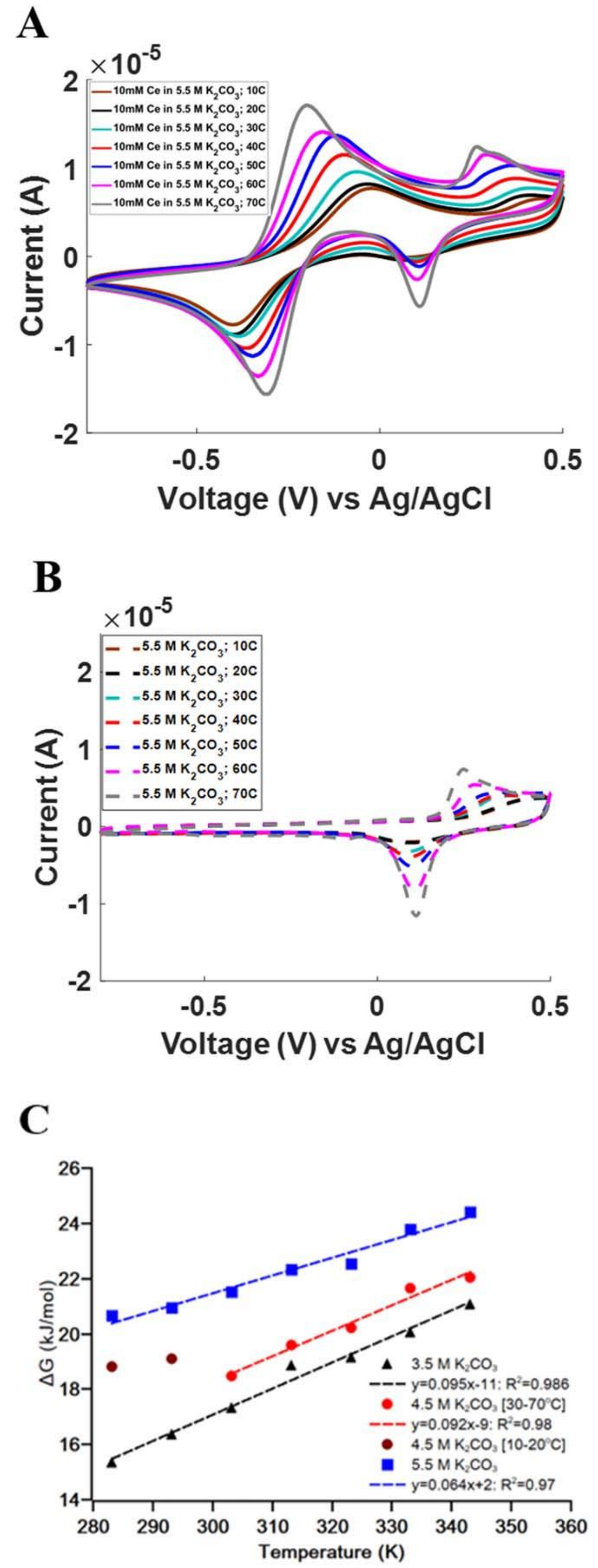

Figure 4. (A) The cyclic voltammograms of 10 mM Ce in 5.5 M K_2CO_3 at 10 °C–70 °C at 100 mV s^{-1}. (B) The cyclic voltammograms of 5.5 M K_2CO_3 at 10 °C–70 °C at 100 mV s^{-1}. (C) The relationship between ΔG and temperature of 10 mM Ce with variable K_2CO_3 concentration at 10 °C–70 °C.

carbonate-hydroxide complex. This complex is more thermodynamically favorable to form than the homoleptic cerium hydroxide species based on the computational studies (27 kcal mol^{-1} lower, *vide infra*). This heteroleptic complex can potentially precipitate out of solution, thus reducing the amount of Ce available in the solution with each additional scan—ultimately affording an increase of Δ E and a decrease in electron transfer kinetics as shown in Table I. The decrease of $E_{1/2}$ might be attributed to the increased stability of cerium(IV) carbonate-hydroxide complex.[36,37]

Temperature.—The solution temperature was increased to allow higher solution carbonate concentrations and afford further stabilization of tetravalent cerium. A preliminary study showed the $E_{1/2}$ of 10 mM Ce in 6 M K_2CO_3 prepared at 60 °C is −249 mV which is lower than the $E_{1/2}$ of 10 mM Ce in 5.5 M K_2CO_3 at room temperature (−223.5 mV), as shown in the K_2CO_3 section. This decrease can be attributed to both temperature and concentration effects as the $E_{1/2}$ of 10 mM Ce in 5.5 M K_2CO_3 at 60 °C is −246.5 mV, so a temperature study was done to determine the impact of temperature on the $E_{1/2}$ of 10 mM Ce in 3.5 to 5.5 M K_2CO_3 at the temperature range from 10 °C–70 °C. The results are shown in Fig. 4, S.3, Tables II and S.I.

The $E_{1/2}$ decreases with increasing temperature, indicating a lower potential is required for Ce(III) to be oxidized at higher temperatures. This is in agreement with what has been previously reported.[23] This observation has been seen in 3.5 M to 5.5 M K_2CO_3. It should also be noted that the $E_{1/2}$ decreased with concentration at the temperature range studied in this work. As shown in Table S.I, the Δ E values decreased with temperature as expected since the greater thermal energy increases the likelihood for a Ce(III)/(IV) complex to overcome the activation barrier for electron transfer and changes in the coordination environment. Therefore, the oxidation of Ce is more kinetically favorable at high temperatures This observation is consistent with all K_2CO_3 concentrations studied in this work.

The thermodynamic properties (Δ H, Δ S and Δ G) can also be obtained at various CO_3^{2-} concentrations based on the temperature dependence study, Eqs. 3 and 4.

$$\Delta G = -nFE_{1/2} \tag{3}$$

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

The resultant Δ H and Δ S at various CO_3^{2-} concentrations calculated from the linear fit of Fig. 4C are shown in Table III. As shown in Table III, the error associated in Δ H is consistent with thermodynamic parameters assessed through the van't Hoff approach, which can have experimental limitations due to the multiplicity of experiments needed to derive a single enthalpy value, as well as the considerable extrapolation associated with finding the intercept at absolute zero. However, the data suggests oxidation of Ce(III) becomes more endothermic at higher CO_3^{2-} concentrations. The values of Δ S are negative with smaller associated uncertainty. The increase in reaction favorability, in the face of unfavorable reaction heats, indicates the oxidation reaction could be generating a substantially more ordered product. The more ordered product could be due to an increase in Ce coordination number with the increased charge density. This observation is consistent with the computational result as described below.

To support assessment of the Ce species in concentrated media, computational modeling was completed of twenty-one different cerium-carbonate compounds (complete list provided in SI). Results of this effort suggest the Ce(III) complex in concentrated CO_3^{2-} media is the tetracarbonato species, $Ce(CO_3)_4^{5-}$, which has been reported previously, Fig. 5A.[24,44] The formation of a heteroleptic Ce(III) carbonate-hydroxide complex is 9.2 kJ mol^{-1} higher energy than $Ce(CO_3)_4^{5-}$ making it energetically unfavorable. The CO_3^{2-} ion has stronger complexing power compared to the ClO_4^- and the computational results indicate the CO_3^{2-} ion is likely to be coordinated to the Ce metal center in a bidentate fashion, also

Table II. $E_{1/2}$ of 10 mM Ce with variable K_2CO_3 concentration.

Temperature (°C)	$E_{1/2}$ at 3.5 M K_2CO_3 (mV)	$E_{1/2}$ at 4.5 M K_2CO_3 (mV)	$E_{1/2}$ at 5.5 M K_2CO_3 (mV)
10	−159	−195	−214
20	−169.5	−198	−217
30	−179.5	−191.5	−223
40	−195.5	−203	−231.5
50	−198.5	−209.5	−233.5
60	−208	−224.5	−246.5
70	−218.5	−228.5	−253

Table III. The thermodynamic data of 10 mM Ce with variable K_2CO_3 concentration.

[K_2CO_3] (M)	Δ H (kJ/ml)	Δ*S* (J/K mol)
3.5	−11 ± 2	−95 ± 5
4.5[a)]	−9 ± 3[a)]	−92 ± 8[a)]
5.5	2 ± 2	−64 ± 5

a) Only the linear region 30 °C–70 °C was used to calculate ΔH and ΔS.

consistent with previous studies.[44,45] Modeling suggests the Ce(IV) structure is $Ce(CO_3)_4(OH)^{5-}$ which has a calculated change in energy, ΔE_{calc}, and change in entropy, ΔS_{calc}, of -420 kJ mol^{-1} and -74.6 J mol^{-1}*K^{-1}, respectively, for its formation from $Ce(CO_3)_4^{5-}$, Fig. 5. The OH^- could be introduced from the deprotonation of water by CO_3^{2-} or the oxidation of water at high pH. The addition of OH^- to tetravalent f-block metal complexes in carbonate media has also been observed with berkelium(IV).[46] The ΔS_{calc} is in good agreement with the experimental data. The large difference in calculated vs experimentally observed enthalpies could be attributed to the limited computational consideration of solvation or the lack of K^+ counterions. Another Ce(IV) complex with a second OH^-, $Ce(CO_3)_4(OH)_2^{6-}$, had an almost identical ΔE_{calc} of -421 kJ mol^{-1}, but the ΔS_{calc} was calculated to be -311 J mol^{-1}*K^{-1} which is far from the experimental values. Other Ce(III) and Ce(IV) structures were considered, but they were found to be higher energy and thus unlikely to be formed. The coordinates and energies of all complexes considered are included in the Supporting Information (SI).

Modelling suggests the Ce(IV) structure is different than the structure proposed in other literature considering lower concentration carbonate media ($Ce(CO_3)_6^{8-}$).[23] This discrepancy is likely due to Larabi-Gruet et al. using an excess of HCO_3^-. This excess will almost entirely eliminate any OH^- at their lower CO_3^{2-} concentration (about 1 M Na_2CO_3). This lack of OH^- prevents the formation of any OH^- containing heteroleptic complexes as compared to the concentrated CO_3^{2-} media with more OH^- available and increased the possibility to form heteroleptic carbonate-hydroxide complex as indicated from computational modeling. The formation of homoleptic vs heteroleptic complexes may also explain the difference in electronic reversibility of the Ce(III)/(IV) couple in Larabi-Gruet et al.'s findings at room temperature, with around 1 M Na_2CO_3 and 0.1 M $NaHCO_3$,[23] as compared to the quasi-reversible couple observed here. Extrapolating the Δ H and Δ S obtained at higher CO_3^{2-} concentration to 1 M CO_3^{2-}, Fig. S.3, the resultant Δ H and Δ S is -28.5 kJ mol^{-1} and -138 J K^{-1}*mol^{-1} respectively. Although the resultant value of Δ H is different than the literature value of -70 kJ mol^{-},[23] it is consistent in being endothermic. Unfortunately, the inherent uncertainty of the extrapolated result prevents any conclusions on the possible existence or role of heteroleptic complexes. The resultant Δ S is similar to the literature value which is -154 J K^{-1}*mol^{-1} and this could potentially indicate the entropic changes of oxidation are similar between high and low CO_3^{2-} concentration, but the large uncertainty associated with the extrapolation prohibits any conclusive statement. The nonlinearity of thermodynamic parameters at different carbonate concentrations might be due to formation of different Ce (IV) complexes, including $Ce(CO_3)_4^{4-}$, and when [CO_3^{2-}] increase, the pH of the solution increase which increase the likelihood of formation of $Ce(CO_3^{2-})_4(OH)^{5-}$.

Stability.—The stability and chemical reversibility of Ce(IV) complexes in CO_3^{2-} media have not been discussed in any previous studies. This section will focus on evaluating the stability and chemical reversibility via chronoabsorptometry experiments. This was done by combining controlled potential electrolysis with spectroscopy as the spectroscopic features between Ce(III) and Ce(IV) are different, Fig. 6A. The initial potential was set to +0.181 V to ensure all the Ce species were oxidized to Ce(IV) and the potential was subsequently changed to −0.579 V to ensure all the Ce species were reduced to Ce(III), Fig. 6B. As shown in Fig. 6B, the absorbance at 312.7 nm was chosen as the Ce(IV) species as it is the only absorbing

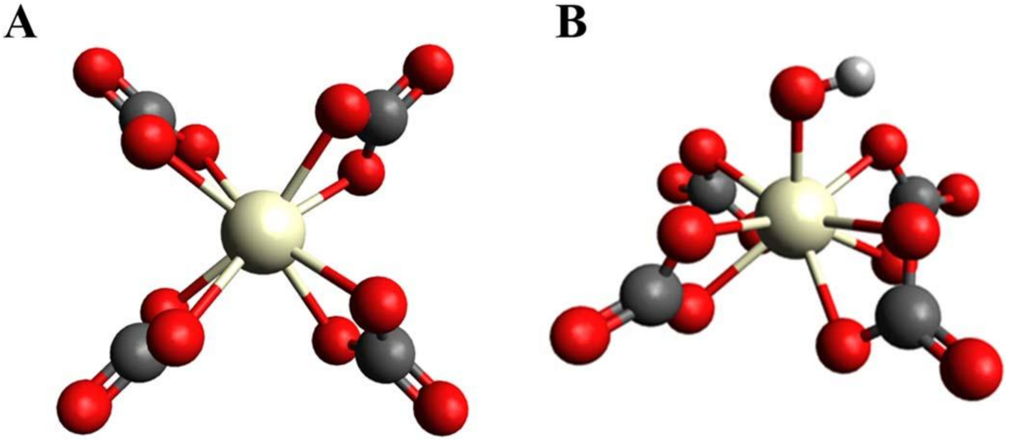

Figure 5. The proposed structure of (A) Ce(III) complex, $Ce(CO_3)_4^{5-}$ and (B) Ce(IV) complex, $Ce(CO_3)_4(OH)^{5-}$.

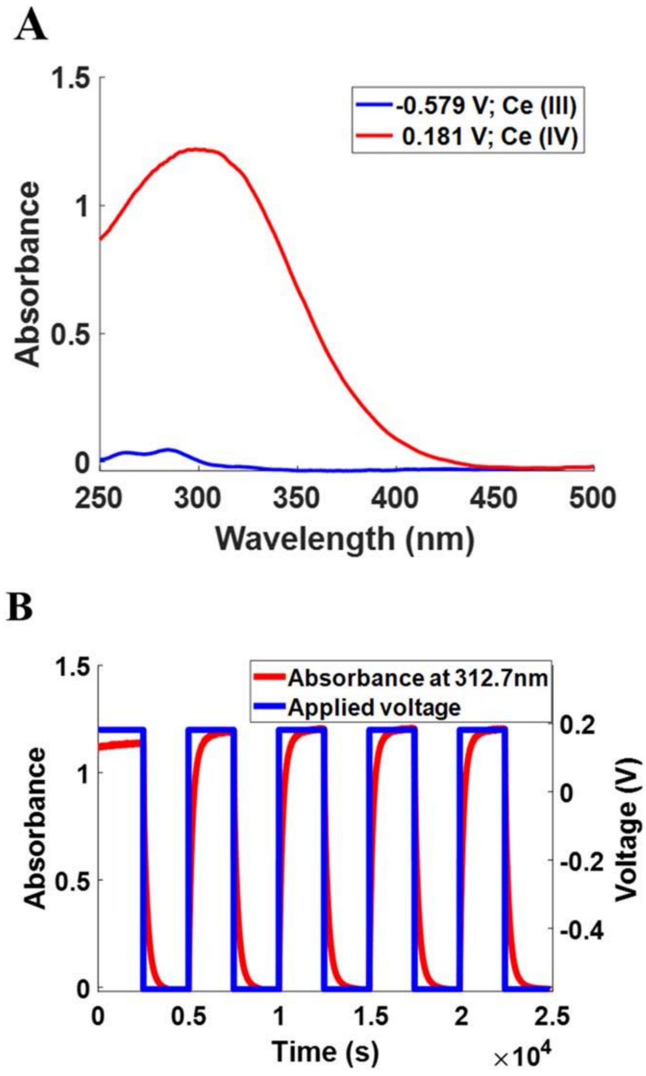

Figure 6. (A) The representative spectra of 1 mM Ce(III) and Ce(IV) in 5.5 M K_2CO_3 which are collected at −0.579 V and at 0.181 V respectively. (B) The chronoabsorptometry result at 312.7 nm of 1 mM Ce in 5.5 M K_2CO_3. The potential was switched between 0.181 V and −0.579 V for five cycles, each potential was held for 41 min.

species at this wavelength. The reversibility of the change in absorbance does not degrade over multiple chronoabsorptometry cycles which indicates the Ce(IV) complex in carbonate media is chemically reversible and stable over time since the Ce can be completely converted between trivalent and tetravalent state multiple times.

The repeated cycling of potential as shown in Fig. 6B allows a determination of the diffusion coefficient by fitting the absorbance to Eq. 5, where A is absorbance, ε_0 is the molar absorptivity, D is the diffusion coefficient, C is the concentration of the analyte, and t is time. This result is independent from the diffusion coefficients calculated from CV results, albeit with a higher uncertainty and a significant potential for misinterpretation. The potential for misinterpretation is due to the subjective nature of identifying the time at which there is a transition from microscopic scale effects at earlier points to the macroscopic scale at later times where diffusion is more relevant. At later times, the Ce(III) and (IV) is oxidized and reduced in the bulk of the solution instead of in or near the pores of electrodes and gives a better comparison to the result of CV because diffusion is the rate limiting process. Including too many early points would dramatically increase the apparent diffusion coefficient by up to three orders of magnitude. With this in mind, a calculation of diffusion coefficients fitted only to absorbances collected after 900 s gave values for Ce(III) and Ce(IV) of 4.1×10^{-8} and 5.5×10^{-8} cm^2s^{-1}, respectively. These values are reasonably close to those measured by CV, especially for Ce(IV), but are less accurate than the CV calculated values due to the number of factors impacting the spectroscopic signature as a function of time that are not related to the diffusion coefficient.

$$A = \frac{2\varepsilon_0 D^{\frac{1}{2}} C t^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \qquad [5]$$

Praseodymium and Terbium (Pr and Tb).—The optimal solution conditions to lower the $E_{1/2}$ of Ce include higher CO_3^{2-} concentrations and higher temperatures. Therefore, these optimal solution conditions were applied to Pr and Tb in CO_3^{2-} to attempt to lower their $E_{1/2}$ to within the thermodynamic domain of water stability. Attempts were made to oxidize Pr and Tb in the optimal solution conditions via cyclic voltammetry, chronoabsorptometry and chemical oxidation. Consistent with earlier reports, chemical oxidation of Pr and Tb to their tetravalent states using ozone at 5.5 M K_2CO_3 and room temperature was possible.[18] However, the electrode potential to oxidize Pr(III) and Tb(III) as the carbonato complexes in the optimal solution conditions was still not low enough to fall within the water stability window. This significantly impeded collection of even qualitative cyclic voltammograms. The spectroelectrochemical data might indicate the presence of Tb(IV) but no conclusive statement can be made due to the low signal to noise ratio. The details of the electrochemical study and chemical oxidation of Pr and Tb can be found in the SI. The collected UV–vis spectra of Tb (IV) shown in Fig. S.11 was similar to the literature.[18] Recent reports have noted the ability to complete bulk electrolysis of Tb(III) to Tb(IV) in carbonate, nitrate and periodate media.[22]

Temperature dependence studies and, associated thermodynamic investigations, provide some limited ability to predict under what temperatures tetravalent Pr and Tb might be stable in 5.5 M K_2CO_3 media. Assuming the shift in the Ce(III/IV) couple is a reasonable proxy for predictions of Pr and Tb chemistry, this study observed a maximum shift for the Ce(III/IV) couple of 1.72 V going from 1.5 V (vs Ag/AgCl) in 1 M $HClO_4$ media at 25 °C to −0.22 V (vs Ag/AgCl) in 5.5 M K_2CO_3 at 25 °C. Since the K_2CO_3 electrolyte seems stable to up to +1 V, quantitative, electrochemical Tb and Pr oxidation may have been supported if the reported literature (III/IV) couples were $\leq$ 2.72 V. Since the Pr and Tb couples are reported at 3.0 V (vs Ag/AgCl) and 2.9 V (vs Ag/AgCl), respectively, an approximate 0.18 V of stabilization is required. Extrapolating the findings of the temperature study, this could potentially be achieved at ~295 °C, however such conditions are incompatible with aqueous chemistry at atmospheric pressure. Carbonate molten salts might be a potential avenue for continued investigation of this system. Alternatively, ability to oxidize Tb and Pr chemically, but not electrochemically, suggests more thorough evaluation Tb and Pr oxidation kinetics and derived mechanisms could provide means to stabilize these exotic oxidation states.

Conclusions

Previous studies have shown the formal potential of lanthanides (Ce(III)/(IV), Pr(III)/(IV) and Tb(III)/(IV)) is lower in concentrated CO_3^{2-} media than the $HClO_4$ media. However, the actual influence of solution conditions on the potential required to oxidize lanthanides has not been fully examined. Therefore, this work mainly focused on evaluating the solution effects including CO_3^{2-}, lanthanide species, OH^- concentration and temperature on the $E_{1/2}$ of Ce (III)/(IV). It was found that higher CO_3^{2-} concentration and temperature will lower the $E_{1/2}$ of Ce in CO_3^{2-} media. It was also found that the Ce(IV) complexes in CO_3^{2-} media are chemically reversible and stable. This optimal solution condition was applied to

Pr and Tb, but the required electrode potential is still higher than the water stability window which greatly affects the quality of the data. Therefore, no conclusive evidence can be collected to indicate the presence of Pr(IV) and Tb(IV) via chemical or electrochemical oxidation. This would lead to the recommendation to investigate the Ln(III) carbonato complexes in non-aqueous media which includes organic media and molten salts.

The coordination environment of Ce(III) and Ce(IV) complexes has been evaluated in this work with the aid of computational studies. The computational work agrees with the experimental results and literature in that the oxidized complex has a higher coordination number than the reduced complex leading it to be less entropically favorable than the reduced complex, but the identity of the computationally proposed Ce(IV) structure, $Ce(CO_3)_4(OH)^{5-}$, differs from that proposed in the literature, $Ce(CO_3)_6{}^{8-}$. This can be attributed to a lower $CO_3{}^{2-}$ concentration (about 1 M Na_2CO_3) and the addition of $HCO_3{}^-$ than was used in the other studies which results in a lack of OH^- and an inability to form heteroleptic cerium (IV) carbonate-hydroxide complexes.

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ORCID

Poki Tse https://orcid.org/0000-0003-2901-9509
Nathan P. Bessen https://orcid.org/0000-0003-2980-6107
Samuel A. Bryan https://orcid.org/0000-0002-8826-0880
Jenifer Shafer https://orcid.org/0000-0001-9702-1534

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