

## **Electrochemical redox processes involving soluble cerium species**

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### **Abstract**

Anodic oxidation of cerous ions and cathodic reduction of ceric ions, in aqueous acidic solutions, play an important role in electrochemical processes at laboratory and industrial scale. Ceric ions, which have been used for oxidation of organic wastes and off-gases in environmental treatment, are a well-established oxidant for indirect organic synthesis and specialised cleaning processes, including oxide film removal from tanks and process pipework in nuclear decontamination. They also provide a classical reagent for chemical analysis in the laboratory. The reversible oxidation of cerous ions is an important reaction in the positive compartment of various redox flow batteries during charge and discharge cycling. A knowledge of the thermodynamics and kinetics of the redox reaction is critical to an understanding of the role of cerium redox species in these applications. Suitable choices of electrode material (metal or ceramic; coated or uncoated), geometry/structure (2-or 3-dimensional) and electrolyte flow conditions (hence an acceptable mass transport rate) are critical to achieving effective electrocatalysis, a high performance and a long lifetime. This review considers the electrochemistry of soluble cerium species and their diverse uses in electrochemical technology, especially for redox flow batteries and mediated electrochemical oxidation.

**Keywords:** cerium, electrochemical engineering, filter press reactor, mediated electrochemical oxidation, redox flow battery.

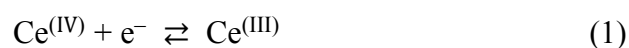
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(Approx. 18,000 words, 4 tables, 17 figures and 237 references).

## 1. Introduction

The electrochemistry of cerium in aqueous, acidic solution is important in a number of electrochemical applications. Cerium, the most abundant and inexpensive of the lanthanide elements and rare earth metals [1] is normally used for aqueous electrochemistry in acid media, where it often participates via the redox reaction:



The Ce(IV) ion is a strong oxidant which is capable of facile electrochemical regeneration. It is classically used in volumetric analysis, particularly in redox titrations. In contrast to vanadium, dichromate, bromate and permanganate ions, cerium ions have lower toxicity and pose no specific environmental risk [2,3]. Cerium salts have moderate cost and are available commercially [4]. Ce(IV) has numerous applications as a prepared reagent, for instance, ammonium cerium(IV) nitrate is used in many organic synthesis reactions involving oxidation as well as Brønsted and Lewis acid catalysis [5]. Binnemans has published a comprehensive review of the application Ce(IV) compounds [6], discussing their use as versatile reagents for a myriad of organic reactions due to their ability to promote radical reactions, functionalize alkenes and catalyse esterifications. Other uses are demonstrated by the ability to remove protecting groups, split organometallic compounds, and catalyse oxidation by bromate ions, peroxides and molecular oxygen as well as initiation of radical polymerization. However, the important scalable electrochemical applications of Ce(IV) regeneration in aqueous solutions have so far been considered partially in the literature and no attempt has been made to bring together these technological expertise from an electrochemical engineering perspective or to describe the factors that govern their

performance. A general scheme of some known and potential applications of the Ce(III)/Ce(IV) and the two main drivers of its efficiency is shown in Figure 1.

Industrial electrochemical processes can have several advantages over chemical treatments [7], including high energy efficiency, operation near ambient temperature and pressure, and minimal use of toxic solvents. Moreover, electrochemical treatment has been extensively applied to environmental remediation [8,9]. The electrogeneration of Ce(IV) in aqueous electrolytes have found use in synthesis, cleaning, decontamination, gas scrubbing and energy storage. Many applications are found in mediated electrochemical oxidation (MEO) of organics, e.g. oxidation of toluene or xylenes to benzaldehydes [10], polyaromatic compounds to quinones [11], the oxidation of naphthalene derivatives to tetrahydroanthraquinone [11] and vitamin K<sub>3</sub> [12], as well as the destruction of organic contaminants, e.g. [13]. Ce(IV) can be recovered and reused efficiently and has many advantages when compared with other MEO species such as Ag(II)/Ag(I) or Co(III)/Co(II) when used in batch or continuous reactors: it does not form chloro-organic compounds and water oxidation rate is low. In a closed acidic environment it completely destroys organic compounds to CO<sub>2</sub> and water, without harmful emissions.

Electrochemical engineering of these operations has also seen important developments, including scale-up of Ce(IV) regeneration from laboratory batch reactors to continuous processes in filter-press reactors, e.g. [11]. Reaction media have evolved to increase the concentration of cerium using methanesulfonic acid (MSA) in place of sulfuric acid [10], and the importance of impurity control in industrial electrolytes has been noted [14]. Among the evaluated electrode materials, 3-D platinized titanium (e.g., in the form of a platinised

titanium mesh) has shown the highest reliability, particularly in comparison with 2-D electrodes susceptible to oxygen evolution. Cost-reduction and optimized performance can be expected from studies of mass transport and the active area of various electrode structures, while fast prototyping techniques such as 3D printing offer possibilities for realising cost effective structures from diverse electrode materials and forms at a variety of scales.

China presently accounts for 97% of the rare earths production, creating some market strain and concerns of restricted supply [15]. Furthermore, the extraction process from monazite and bastnasite via selective precipitation has severe environmental consequences [1,16]. These reasons have emphasized the need for cerium recycling [17], creating opportunities for electrochemical technology developments.

## **2. The Ce(IV)/Ce(III) redox couple**

### **2.1 The history of developments in soluble cerium species**

As seen in Figure 2, the electrochemical properties of cerium in aqueous solution have been continuously exploited over more than 150 years, from deployment in laboratory volumetric analysis to industrial process plants. Many applications have been proposed and some abandoned, while recent advances open new opportunities. The central use of Ce(IV) as a selective redox mediator in commercial organic synthesis dates back to dyestuffs manufacture in the early 20th century as does its use as an oxidation catalyst in organic synthesis [19]. Its brief use in photography dates from the same period [19]. The use of cerium as an oxidant in classical volumetric analysis began much earlier, with titrations first performed by Lange in 1861 [18]. Cerimetry using colour indicators was introduced in 1928 by Willard and Young [18], followed by coulometric titrations in 1951 due to Furnan *et al.*

[20]. The electrolytic regeneration of Ce(IV) began in the late 1960s for nylon production [23]. Such applications were limited due to the low solubility of cerium ions in sulfuric acid and much research was focused on extraction of organic synthesis products from two-phase reaction media. During the 1970s and 1980s, cerium oxidant solutions entered the fields of unwanted organic destruction [24], nuclear decontamination [25], gas scrubbing [27], and analysis involving chemiluminescence [28]. Kreh *et al.* reintroduced MSA as a high solubility medium for cerium ions [10,34], enabling practical electrosynthesis at a time when electrochemical reactors design was rapidly developing. Shortly after this, Harrison *et al.* applied anodic generation of Ce(IV) in MSA for oxidation of naphthalene to naphthoquinone, scaling up successfully to a (initial) 100 tonne per year plant [11]. This provided a proof of concept for the positive half-cell of the Zn-Ce RFB for energy storage [31] and the mediated electrosynthesis of vitamin K derivatives [32]. Currently, environmental concerns encourage the use of recyclable redox mediators and the recovery of rare earths, giving a new impetus to the field. Further examples of development are given in section 6 while possible future applications are discussed in section 8.

## **2.2 The speciation and chemistry of cerium in aqueous solvents**

As shown in the Pourbaix diagram of Figure 3, cerium ions are soluble in strong acids while insoluble hydroxyl complexes are stable at neutral and basic pH [36]. Other insoluble salts include carbonates, phosphates, fluorides and oxalates [16]. Cerium ions will have different solubility in different acids. It is worth mentioning that the Pourbaix diagram is based on purely thermodynamic properties and does not represent the kinetic characteristics of the ions. Both sulfuric acid and MSA solutions are suitable for electrochemical applications but the solubility of cerium is much higher in MSA [10,34]. The solubility limits of Ce(III) and

Ce(IV) methanesulfonates are approximately  $2.4 \text{ mol dm}^{-3}$  and  $1.0 \text{ mol dm}^{-3}$ , respectively [34] as shown in Figure 4. This, along with its high stability, low vapour pressure, mild corrosivity and low toxicity [37], has made aqueous MSA a preferred media for cerium redox processes. (The use of hydrochloric and nitric acids is strongly discouraged due to the generation of  $\text{Cl}_2$  and  $\text{NO}_x$  gases, respectively, along with their high vapour pressure and corrosivity. Perchloric acid can produce explosive compounds and is not used in the electrochemical industry.) Ce(IV) solutions are typically obtained by electrolysis of Ce(III); the solutions can be prepared by neutralization of cerium(III) carbonate suspensions with acid. The carbonate is available as trihydrated or octahydrated salts, the latter being more soluble.

Regarding aqueous electrochemistry, the Ce(III)/Ce(IV) redox couple has the most suitable properties among lanthanides, which show diverse standard electrode potentials, (Table 1), in spite of their similar chemical properties. Several of them have standard electrode potential values well beyond the decomposition of water, such that their reduction to metals is performed from molten salts [39]. Ionic liquids are often proposed as alternative solvents, but the solubility of lanthanides in these media is extremely limited [40].

Cerium ions exhibit complicated solution chemistry due to their high susceptibility to complexation, resulting from the influence of the  $4f$  electron. This is typical of the lanthanides group, which are characterized by the formation of hydrated complexes in solution and favoured complexation with donor anionic ligands of high electronegativity [41]. The location of the  $f-d$  electron transition bands and charge transfer bands in the spectrum are responsible to the lack of colour of Ce(III) and the Ce(IV) colouration,

respectively [42]. Ce(III) absorbs in the infrared and the ultraviolet spectral region, where its  $f-d$  electron transition band is located. The yellow-orange colour of Ce(IV) ions is the result of the movement of a portion of the ultraviolet absorption band into the visible region of the spectrum [42].

The predominance of cerium species in acid solutions as well as the precipitation of salts depends on both counter-ion and proton concentrations. In some cases, these cerium complexes are metastable. Ceric ions do not form complexes with perchloric ions in solution, forming instead hydrolysed species that can reduce water molecules [43]. In contrast, Ce(III) and Ce(IV) ions will form a series of complexes with other acids, many of them anionic. In nitric acid, both ions will associate with up to 5 nitrate groups [44]. Cerium ions form strong bond with sulfates, resulting in a relatively low solubility. Ce(III) in sulfate solutions can be found as  $[\text{CeSO}_4]^+$  [45,46],  $[\text{Ce}(\text{SO}_4)_2]^-$  [47], or  $[\text{CeHSO}_4]^{2+}$  [48], the latter predominating at sulfuric acid concentrations over  $1.7 \text{ mol dm}^{-3}$ . Spectrophotometric analysis indicates that Ce(IV) forms the complexes  $[\text{CeSO}_4]^{2+}$ ,  $[\text{Ce}(\text{SO}_4)_2]$ , and  $[\text{Ce}(\text{SO}_4)_3]^{2-}$  with increasing sulfate concentration [49]. Speciation diagrams of Ce(III) and Ce(IV) are shown in Figure 5. The strong interaction with sulfates results in negative enthalpies of solution for  $\text{Ce}_2(\text{SO}_4)_3$  and  $\text{Ce}(\text{SO}_4)_2$  salts, their solubility being reduced with rising temperature [46,51]. According to Vijayabarathi *et al.* [52], Ce(III) exists as  $[\text{CeCH}_3\text{SO}_3]^{2+}$  and  $[\text{Ce}(\text{CH}_3\text{SO}_3)_2]^+$  cations in MSA solutions, while Ce(IV) is present as  $[\text{CeCH}_3\text{SO}_3]^{3+}$  or  $[\text{Ce}(\text{CH}_3\text{SO}_3)_2]^{2+}$  cations. In alkaline carbonate solutions Ce(IV) can be present as  $[\text{Ce}(\text{CO}_3)_6]^{8-}$  and Ce(III) as  $[\text{Ce}(\text{CO}_3)_4]^{5-}$  [53].



### 2.3 The aqueous electrochemistry of cerium

In general, the Ce(III)/Ce(IV) redox reaction is characterized by: a) a charge transfer that involves several steps, b) dissimilar values of its anodic and cathodic charge transfer coefficients, and c) a behaviour highly dependent on coordination with ligands. Relatively fast kinetics permit practical use of the reaction, although the reduction tends to be slower than the oxidation and voltammograms are irreversible in several acid media, noting that in some cases (e.g. MSA, sulfuric acid) oxygen evolution hinders clear definition of an oxidation peak.

Both thermodynamic and kinetic parameters of the cerium redox reaction are significantly affected by the interaction with ligands. Thermodynamically, the main effect is a shift in the standard electrode potential of the reaction due to the presence of ligands and the strength of the interaction. Changes in the coordination sphere at the electrode surface are accompanied by a more positive electrode potential [54]. A clear illustration of this relationship is provided by the potential values seen in different acids media, in Table 2.

The diffusion coefficient of cerium ions is reduced due to larger size of the coordination and solvation sphere, making the reaction less reversible and increasingly dependent on mass transport. Secondly, at least one time-consuming step is introduced into the reaction due to reorganization of ligands at the electrode surface. As shown in Figure 6, Xie *et al.* [57] have proposed that the configuration of the cerium complex changes at the electrode surface, affecting the kinetics in industrial MSA-based electrolytes. Furthermore, Ce(III) and Ce(IV) have different ionic radii of 114 pm and 97 pm, respectively [16].

These effects are more evident in sulfuric acid, where the variation in the formal potential for Ce(III)/Ce(IV) is a consequence of complex equilibria [58]. Paulenova *et al.* [51] explained the slow reduction kinetics and potential shift of the cerium redox reaction in sulfuric acid solutions in terms of dissimilar ligand bonding of Ce(III) and Ce(IV) with sulfate ions, the ceric ion complex being more stable. The electrode potential shifts to negative values as the concentration of sulfuric acid is increased. Comparison to the reaction in nitric acid confirms the dependence on coordination chemistry. Pletcher and Valdés [59] found that the formal potential of the cerium redox reaction was not affected by the concentration of nitrate or protons, as indicated by same number of nitrate ligands being present in the oxidized and reduced ions.

Similarly, the observed formal potential shifts and relative slow kinetics of the Ce(III)/Ce(IV) redox reaction in MSA are a consequence of the formation of complexes [52]. Xie *et al.* [56] stated that different complexation of Ce(III) and Ce(IV) with methanesulfonate ions and ligand reorganization at the electrode interface are responsible for the slow kinetics. The same authors have suggested that, if the cerium-methanesulfonate complex has a tetrahedral configuration, then the reaction at the interface would necessitate its transformation into a pyramidal configuration before electron transfer, with a corresponding energy demand [57]. The dependence of the thermodynamics and kinetics of the cerium redox reaction on its associated ligand chemistry and ligand reorganization is a central topic in the review of the electrochemistry of cerium organic complexes by Piro *et al.* [67] Ce(IV) does not seem to respond in the same way as transition metals and actinides to organic ligands commonly used to stabilize higher oxidation states. This might suggest restrictions in the use of complexing agents/additives or Ce-based polyoxometalates in industrial electrolytes.

The composition of the electrode will also determine the electrochemical response of the cerium redox reaction. Platinum electrodes give a good response for voltammetric analysis, although they are sensitive to oxide layer formation on their surface, whose thickness reduces the rate of the reaction [60-62]. Glassy carbon and platinum [63,64] give well-defined voltammograms in sulfuric acid with cerium concentrations in the order of  $1 \text{ mmol dm}^{-3}$ . Gold and iridium are affected by the formation of surface oxide layers [63] and corrosion by Ce(IV) in the case of gold [64]. Glassy carbon allows to obtain more reversible voltammograms in nitric acid solutions [59], but suffers from corrosion in acids at the concentration required in the cerium redox flow battery [51].

## **2.4 Oxygen evolution**

The main parasitic reaction affecting Ce(III)/Ce(IV) couple is the oxidation of water with evolution of  $\text{O}_2$ , which is thermodynamically favoured at this redox potential. The oxidation of Ce(III) is affected the most and this can produce efficiency losses and limit the operational current density in reactors, particularly when planar electrodes are used instead of three-dimensional ones [33,65,66]. Low electrolyte flow rates can also allow gas bubbles to remain near the electrode thus increasing the resistivity of the electrolyte near its surface [67]. Platinum electrodes show intense electrocatalysis for oxygen evolution at applied potentials more positive than +1.8 vs. SHE in Zn-Ce battery electrolytes [68], although the reaction is hindered by increasing MSA concentration [69]. Oxygen evolution has an exchange current density in the order of  $2 \times 10^{-10} \text{ A cm}^{-2}$  at Pt in highly pure sulfuric acid solutions [70]. In contrast, the Ce(III)/Ce(IV) redox reaction has a reported exchange current density at Pt of  $3.7 \text{ A cm}^{-4}$  in a typical RFB electrolyte (from Tafel analysis) [71] but also  $1.32 \text{ mA cm}^{-2}$  in a more dilute MSA solution [56]. Clearly, these magnitudes are difficult to reconcile. The

competition between anodic Ce(III) oxidation and oxygen evolution, which is important to current efficiency of cerous ion oxidation, the selectivity of cerium mediated electrochemical synthesis and the energy efficiency of redox flow batteries deserves more detailed consideration.

### 3. Electrode kinetics

Voltammetric studies on the kinetics of the Ce(III)/Ce(IV) redox reaction and detailed kinetic data are shown in Table 3. Since the earliest studies of redox potential at platinum [21], and kinetic studies at platinum and carbon rotating disc electrodes in sulfuric acid [22], it was noted that the analysis of cerous ion oxidation is difficult by voltammetry and that the charge transfer coefficients are  $<0.5$ . Experiments performed at gold and platinum electrodes in perchloric, nitric and sulfuric acid revealed hysteresis and sensitivity of the kinetic parameters of the reduction to the formation of oxide films [74] and oxygen adsorption [73], explaining the cathodic charge transfer value of 0.25 at platinum. Similar surface effects were observed at iridium electrodes but not at glassy carbon, their reduction transfer coefficient being also close to 0.25 [63]. The kinetics of Ce(III) oxidation were first studied by Bishop and Cofré [64]. The authors reported that the reaction rate was higher at glassy carbon than at platinum, with anodic charge transfer coefficients of 0.49 and 0.30, respectively.

In order to correct for the presence of surface platinum oxides, Randle *et al.* [60-62] determined the anodic and cathodic reaction rate and charge transfer coefficients at carefully standardized platinum surfaces. It was confirmed that the reaction rate is of first order at overpotentials under 10 mV and at millimolar concentrations. Ce(III) oxidation shows an apparent reaction order of  $< 1$  at higher concentrations. In sulfuric acid the anodic and

cathodic charge transfer coefficients for platinum covered with a layer of oxides were close to 0.60 and 0.20, respectively. Nzikou *et al.* have provided standard rate constants, charge transfer coefficients and diffusion coefficients for both Ce(III) and Ce(IV) at platinum over a range of sulfuric acid concentrations, between 0.1 to 5.0 mol dm<sup>-3</sup> [77]. The formation of oxides was minimized in more practical conditions, yielding anodic and cathodic charge transfer coefficients were 0.29 and 0.31 in 1.0 mol dm<sup>-3</sup> sulfuric acid. Comparing these results to the work of Randle *et al.*, indicates that the cathodic charge transfer coefficient is decreased by the oxide layer at platinum surfaces.

The study of Ce(III)/Ce(IV) kinetics has been performed in other acid media and electrode materials. The cerium redox reaction is more reversible in nitric acid [59] or at boron-doped diamond electrodes [76]. Kinetic evaluation for different applications has involved: a) RFB in sulfuric acid [50,51,75], MSA [56,68,71], and mixed-acid electrolytes [79-81]; b) MEO [82,83]; gas scrubbing [77]. The kinetics of the Ce(III)/Ce(IV) redox reaction has been further studied for the industrially used MSA electrolytes [52,68,71,79,82]. Detailed kinetic data for MSA-based electrolytes for the Zn-Ce RFB is shown in Table 4, sulfuric acid electrolytes being included for comparison. Figure 7 shows the effect of increasing MSA concentration on the oxidation of Ce(III) at platinum electrodes in an electrolyte of industrial composition. The oxidation current to produce Ce(IV) decreases with the concentration of MSA.

#### **4. Mass transport and diffusion**

Mass transport data of cerium species is available from several rotating disc electrode (RDE) experiments in various media via the Levich analysis. Tables 3 and 4 include the diffusion

coefficients of cerium ions in dilute acids and electrolytes used in redox flow batteries. Recently, the mass transport environment for anodic Ce(IV) generation has been determined as the product of average mass transport coefficient and volumetric electrode area from the limiting current obtained at different electrode structures in filter-press cells [33]. This type of electrode characterization is important for efficient electrochemical reactor design.

Greef and Kiekens first showed that the diffusion coefficient of  $1 \times 10^{-3} \text{ mol dm}^{-3}$  Ce(IV) in  $1.0 \text{ mol dm}^{-3}$  sulfuric acid at  $25^\circ\text{C}$  was  $3.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  [63,74]. Later, Randle showed that the diffusion coefficients of Ce(III) and Ce(IV) ions were similar, with values of  $5.2 \pm 0.3 \times 10^{-6}$  and  $5.0 \pm 0.3 \times 10^{-6}$  in  $0.5 \text{ mol dm}^{-3}$  sulfuric acid at  $25^\circ\text{C}$  [60]. Diffusion coefficients depend on the viscosity of the medium and ionic interactions, so the diffusion coefficient for Ce(IV) determined at platinum electrodes has shown values from  $4.5 \times 10^{-6}$  to  $1.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  on increasing the concentration of sulfuric acid from  $0.1$  to  $5.0 \text{ mol dm}^{-3}$  [77], reaching a value of  $1.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  in  $15 \text{ mol dm}^{-3}$  sulfuric acid at  $25^\circ\text{C}$  [74]. The diffusion coefficient of Ce(III) increases to a maximum value near  $0.5 \text{ mol dm}^{-3}$  sulfuric acid, decreasing with rising acid concentration [77], possibly indicating a change in the ligand conformation. At boron-doped diamond electrodes the diffusion coefficient of Ce(III)  $1.05 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  in sulfuric acid, with lower values of ca.  $5.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  in nitric and perchloric acid [76], in accordance with the value of  $6.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  found by Pletcher and Valdés in nitric acid [59]. The addition of other active species such as sulfosalicylic acid to the solutions appeared to increase diffusion coefficients of cerium ions [86]. An increase of the diffusion coefficient of cerium ions with temperature was observed in an Arrhenius plot in nitric acid [88].

The diffusion coefficients of cerium species in industrially important MSA electrolytes have been considered. Nikiforidis *et al.* found a value of  $2.17 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  for the diffusion coefficient of Ce(IV) via Levich analysis of RDE data in a zinc-cerium redox flow battery electrolyte at 25 °C, which rose to  $4.17 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  at the operational temperature of 50 °C [71]. Figure 8a) presents the limiting current for Ce(IV) reduction at a platinum electrode for the electrolyte of a Zn-Ce RFB at different rotation rates and Figure 8b) the corresponding Levich plot. The diffusion coefficient of  $0.4 \text{ mol dm}^{-3}$  Ce(IV) was  $9.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  at 25 °C for an electrolyte having a kinematic viscosity of  $3.88 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ . The redox reaction was also studied at glassy carbon electrodes in MSA by Devadoss *et al.*, who recorded diffusion coefficients for Ce(III) from 2.7 to  $6.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  in the concentration range of 0.03 to  $0.15 \text{ mol dm}^{-3}$  [84]. Xie *et al.* have determined the diffusion coefficients of cerium species at rotating platinum electrodes in aqueous MSA solutions [56]. Values of  $2.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  and  $5.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  were found for the Ce(IV) and Ce(III) ions, respectively in  $2.0 \text{ mol dm}^{-3}$  MSA. The same authors found that the diffusion coefficient of Ce(III) had a higher value of  $6.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  in a mixed acid medium of methanesulfonic and sulfuric acids [79]. The results from Xie *et al.* showed values nearly one order of magnitude higher, most likely due to the determination method, which used chronoamperometry and the Cottrell equation. In general, the diffusion coefficient varies in the range of  $2.1 - 9.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  if Xie *et al.* values are not considered depending on the authors and the experimental conditions.

## 5. Electrode materials

Platinised titanium mesh is the most common electrode material for the anodic generation of Ce(IV). The 3-D structure and high surface area of this electrode material allow higher conversion rates and current efficiency than 2-D materials in synthesis [11], decontamination

[89], and energy storage [68]. Reticulated  $\text{IrO}_x\text{-Ti}$  porous, 3-D electrodes showed similar benefits [34]. Porous structures such as mesh (Figure 9b) and micromesh (Figure 9c) enhance the performance of electrochemical flow reactors by increasing electrode area and mass transport rates in comparison to plates (Figure 9a). Mean linear electrolyte velocities are also higher, helping to dislodge gas bubbles, and mixing and turbulence are promoted. In the case of noble coatings on titanium substrates, it is important to avoid through porosity in the coatings as this can lead to localised bimetallic corrosion. It is also important to realise that titanium can corrode cathodically via hydride formation.

A number of metals and metal oxides with different catalytic activity towards the  $\text{Ce(III)/Ce(IV)}$  reaction have been studied, mostly in 2-D configuration. For instance, an early evaluation of sheet electrodes gave the following order of performance:  $\text{PbO}_2$ ,  $\text{Pt} > \text{IrO}_x\text{-Ti} > \text{RuO}_x\text{-Ti (DSA)} > \text{glassy carbon}$  [10,34]. Planar  $\text{Pt/IrO}_x$  coatings produced no significant improvement to the ca. 30% efficiency observed at  $\text{Ti-PbO}_2$ , steel-Pb and Sb-Pb alloy electrodes in sulfuric acid [90]. The use of very smooth Pt electrodes in a flow cell resulted in reduction efficiency of  $\text{Ce(IV)}$  formation, in comparison to rougher deposits, probably due to gas bubble effects [91]. In another study [11], higher current efficiencies were observed at Pt-Ebonex and Pt-Ti, followed by  $\text{IrO}_x$  and  $\text{PbO}_2$ . DSA electrodes for oxygen evolution ( $\text{IrO}_2\text{-Ta}_2\text{O}_5$ ) are comparable to the more expensive Pt-Ti [92] and, under battery conditions,  $\text{Pt/IrO}_x$  coatings have shown the highest exchange current densities [71]. Expensive diamond-coated electrodes have also been suggested to decrease oxygen evolution [76,93]. Some of these materials (e.g. Ebonex) could be practical alternatives if they could be coated on 3-D structures, e.g. metal mesh, reticulated vitreous carbon, carbon foam, titanium felts. Gold



electrodes are not considered a suitable alternative due to their susceptibility to corrosion by Ce(IV) [63].

The application of low-cost 3-D carbon electrodes for cerium reactions remains as a challenge. Materials such as carbon felt [94] and carbon paper [95], along their modifications with carbon-based catalytic surfaces, e.g. hierarchical porous carbon [96] and graphene [97], seem promising. Higher current density, improved reversibility of the cerium reaction and reduced oxygen evolution could be potentially achieved. In practice, the electrical connection between carbon felts and the bipolar electrode/current collectors tends to degrade rapidly. The material itself can oxidize, especially in nitric acid electrolytes [98]. Graphitized carbon-polymer composites coated with Pt and Ir oxides were suggested as cost effective bipolar electrodes [31]. Although they promoted fast reaction kinetics, the electrocatalysts deteriorated quickly [71] while the performance of such 2-D electrodes is inadequate. There are relatively few quantitative and comparative studies of electrocatalyst coatings, electrode materials and electrode structures for cerium redox reactions, despite their industrial uses and potential applications.

## **6. Applications**

### **6.1 Mediated electrosynthesis**

Cerium takes part in indirect electrochemical processes via mediated electrochemical oxidation (MEO). In these operations a reactant of interest is oxidized by the electrochemically generated reducing form of the redox mediator with the aim of overcoming low conversion efficiency or low solubility. The reaction between the reactant and the redox mediator can take place in the same solution within the electrochemical reactor (*in-cell*

method) or in an external dedicated non-electrochemical reactor (*ex-cell* method) [6]. Cerium MEO can be represented as [34]:



where R is the reduced form of the mediator, O its oxidized form, S the reactant of interest and P its oxidized product. At industrial scale, the recycled electrolytes require periodic removal of the organic and metallic impurities. The applications of Ce(IV) in MEO synthesis have been previously summarized by Noel *et al.* [99] and Binnemans [6], and discussed in the context of the pharmaceutical industry by Walker [100]. These useful works described the efficiency of various applications but little consideration was given to the effects of electrode structure and mass transport or to the electrochemical engineering of these processes.

The first proposed industrial applications for Ce(IV) electrogeneration in MEO synthesis involved the production of 1,4-dichlorobutane and 1,6-dichlorohexane for nylon manufacture in the presence of methanesulfonate ions [23] and later the synthesis of aromatic aldehydes in a perchloric acid electrolyte (which can be particularly dangerous in large-scale industrial operations) [101]. Due to the requirement of safer conditions and higher concentration of organic compounds, nitric acid was proposed as solvent for anodic Ce(IV) generation, at the cost of noxious NO<sub>x</sub> formation [24]. In order avoid this, Kreysa and Medin produced *p*-methoxybenzaldehyde in a two-phase electrolyte based in sulfuric acid and designed a pilot plant for a stirred batch reactor [102]. Dichloromethane was employed to extract the product from the two-phase reaction mixture. Aiming to develop similar processes, the extraction of

products from dichloromethane and *n*-hexane oxidation by Ce(IV) using tetrabutylammonium and tributylphosphate ions was investigated [59,103], and the regeneration in an undivided cell was achieved with constant extraction of Ce(IV) with ethylhexylphosphoric acid in kerosene [65]. Nevertheless, the use of planar electrodes severely limited the operational current density. Tzedakis and Savall continued the development of the electrosynthesis of *p*-methoxybenzaldehyde in sulfuric acid coupled with dichloromethane extraction, modelling the process [104], and experimentally studied its kinetics, selectivity and operational conditions [105,106]. The kinetics of Ce(IV) regeneration in sulfuric acid in such operations in flow reactors have been recently modeled [107], highlighting the importance of ligand reorganization as a rate determining step.

The mediated electrosynthesis of naphthoquinone is an attractive electrochemical process and, initially, ceric sulfate slurries were generated in sulfuric acid for this purpose [108]. Further development allowed preparing ceric sulfate solutions [109], and the regeneration of slurries was later optimized for a continuous process in an undivided cell [110], although secondary reactions were dominant and the concentration of Ce(IV) was limited to 0.125 mol dm<sup>-3</sup>. Comninellis and Plattner demonstrated that the presence of Ag<sub>2</sub>SO<sub>4</sub> and MnSO<sub>4</sub> as catalysts augmented the efficiency of cerium conversion in these conditions [111], and proposed the calculation of current efficiency loss from the total organic carbon in the recycled electrolyte in MEO processes [112]. Ultimately, a two-step electrosynthesis of naphthoquinone was attempted using Ce(IV) saturated sulfuric acid solutions [90]. The system was taken to a pilot-plant scale, but low current efficiencies of 60% were achieved and high conversion rates could only be obtained at long reaction times, making the process commercially unviable.

A milestone was reached when Kreh *et al.* showed that MSA greatly improved the solubility of Ce(IV) ions, enabling practical electrosynthesis of aromatic aldehydes and quinones by the oxidation of polycyclic aromatic compounds [10,34]. This process was patented under W. R. Grace & Co. [113,114]. (Electrogeneration of Ce(IV) and its high solubility in MSA were suggested in 1968 by McLean [23] but no further developments took place.) As shown in Figure 4, the solubility of Ce(IV) increases with the concentration of MSA reaching a maximum of *ca.* 1.0 mol dm<sup>-3</sup>. In contrast, its solubility in sulfuric acid is 0.125 mol dm<sup>-3</sup> in saturated solutions [109]. The solubility of Ce(III) has a value of 2.1 mol dm<sup>-3</sup> in a solution of 1.0 mol dm<sup>-3</sup> MSA, decreasing with higher of MSA concentration [34]. As a result, naphthoquinone yields of more than 90% were achieved from initial naphthalene concentrations of 0.2 mol dm<sup>-3</sup> in a medium containing 0.2 mol dm<sup>-3</sup> Ce(IV), 3.5 mol dm<sup>-3</sup> MSA and 0.012 mol dm<sup>-3</sup> tetrabutylammonium hydroxide. In order to assess the viability of the process, an industrial operation was modelled [115], considering the two-phase reaction, separation and extraction of products.

In view of possible electrosynthesis of naphthoquinone, the process was further improved by Harrison *et al.* and patented by Hydro-Québec [29,116], who acquired the technology from Grace & Co. (The process is currently licensed under the name CeTECH<sup>TM</sup> by Lonza Group A.G. [32].) In the two-step *ex-cell* method described in Figure 10, an aqueous phase containing the electrogenerated Ce(IV) and an organic phase containing the organic reactant are mixed at high velocity in a dedicated reactor [11]. The general reactions are shown in Figure 11, each molecule of naphthalene requiring 6 electrons for its oxidation [90]. After this step, spent Ce(III) solution is regenerated in the electrochemical flow reactor. The product of the MEO is separated and dried. In this way, the indirect electrosynthesis of

naphthoquinone, anthraquinone and tetrahydroanthraquinone from naphthalene was successfully scaled-up to a 100 tonne per year commercial plant [11]. Although less used now, anthraquinone itself acts as a redox mediator that accelerates the reduction of lignin while preventing cellulose degradation in the Kraft pulping process for paper production [117].

Indian researchers have further developed Ce(IV) MEO in MSA media, applying it to several organic oxidations of industrial interest. Initially, benzoquinone was obtained from benzene with an efficiency of 45% in presence of  $4.0 \text{ mol dm}^{-3}$  MSA at  $75^\circ\text{C}$  with the addition of 0.4% CTAB in to the aqueous phase [83]. Benzene showed high stability towards oxidation by ceric ions in MSA, and only the presence of the surfactant permitted significant benzoquinone yields. The kinetics of the cerium redox reaction in MSA were compared to other acids, also showing the inhibitive role effect of organic impurities and products at the electrodes [52]. Compounds such as toluene, benzaldehyde and naphthaquinone have no effect on the electrode reactions, while *p*-ethoxy toluene and *p*-ethoxy benzaldehyde inhibit them. Authors justified the advantages of two-step electrosynthesis. The alternative use of Mn and Co as redox mediators in MSA was discouraging [82]. Operational conditions for a Ce(IV) generation batch process were also studied [118], showing the advantages of Pt-Ti electrodes and high temperatures. In a summary, Noel *et al.* listed toluene, *p*-amino toluene, *p*-cresol, *p*-chlorotoluene, *o*-and *p*-xylenes and *m*-xylene as other possible reagents [99]. Scaling up work was performed by studying the kinetics and efficiency of batch and flow reactors for Ce(IV) electrogeneration for quinone production in MSA [119]. Using a planar DSA electrode, the batch reactor showed the highest current efficiency for an optimized electrolyte for  $0.8 \text{ mol dm}^{-3}$  Ce(III) in  $2.0 \text{ mol dm}^{-3}$  MSA at  $50^\circ\text{C}$  [92]. The scale-up of *p*-

methoxybenzaldehyde production, which is used in pharmaceuticals and fragrances, realised efficiencies up to 78% at 30 °C with an optimal energy requirement of 0.8 kW h kg<sup>-1</sup> [84].

The latest application of the CeTECH<sup>TM</sup> process involved the commercial synthesis of vitamin K<sub>3</sub> (menadione) was performed by the Lonza Group A.G. with a reported capacity of 400 tonnes per year [32], the general reaction is shown in Figure 12. Ce(IV) is used as a substitute for the toxic chromic acid used in previous industrial methods, required at quantities of 18 kg per kg of menadione [120]. The process is an improved version of the electrosynthesis of naphthoquinone [29,116], including an additional purification step of the cerium-containing electrolyte, as soluble organic compounds affected the efficiency of the redox reaction [14]. The inhibition of Ce(IV) generation in the presence of organic occurs in other media, e.g. it was observed during the oxidation of *p*-methoxytoluene [106]. The improved process was also described for the production of *p*-tolualdehyde. The production of vitamin K<sub>3</sub> was intended for animal nutrition [121], but a patent filed for the treatment of osteolysis in humans using MEO-produced vitamin K compounds (2-methyl-1,4-naphthoquinone derivatives) [122], suggested possible applications in the pharmaceutical industry.

The indirect oxidation of several other organic compounds using Ce(IV) has been performed. For instance, 1,6-pyrenedione [123], unsaturated products of the dimerization of carbonyl compounds [124], monosaccharides [125], poly(vinyl alcohol) [126], salicylidene aminophenols [127], substituted mandelic acid [128], acetoin [129], poly(ethylene glycol) [130], reserpine [131], and the Schiff base 2-hydroxy-1-naphthalidene-anil [132]. Soluble metallic ions can catalyse the oxidation of many organic and inorganic substances by Ce(IV).

Das has reviewed these catalysts [133], which include Ru(III), Ir(III), Mn(II), and Ag(I). Some examples are the oxidation of toluene from benzaldehyde using silver as catalyst [134], the oxidation of formic acid catalysed by Ru(III) [135], and the oxidation of dimethyl sulfoxide was catalysed by Os(VIII) ions [136].

Future developments in mediated electrosynthesis could be derived from revisiting synthesis methods using MSA-based electrolytes, and perhaps by combining MEO processes with supercritical extraction of products from the organic phase [137]. In a competitive market, the optimization of reactor performance and expensive electrode materials, as well as the attention to high value added applications, is essential to successful industrial applications.

## **6.2 Cleaning and surface decontamination**

### ***Nuclear decontamination and decommissioning***

Nitric and sulfuric acid solutions containing Ce(IV) are used as specialized cleaning agents for stainless steel vessels and pipelines in the nuclear industry, having a special role in the decommissioning of nuclear facilities. Pieces of equipment, such as gloveboxes, are also decontaminated in this way. The regeneration of the oxidant in an electrolyser can keep a closed system, minimizing the volume of residual solutions (expensive to treat and dispose). Recently, cerium MEO was found applicable in the decontaminations efforts in the Fukushima Daiichi accident by the Japan Atomic Energy Agency [138], highlighting short decontamination times and recyclability of the solutions up to 15 times. Typically, stripping of dangerous radionuclides from steel components can be done by etching in nitric acid solutions of Ce(IV) [25], and a Japanese patent states that the use of this oxidant in sulfuric

acid greatly reduces the amount of reactant and treatment time [139]. The cooling system of the reactors can be treated by dilute solutions of Ce(IV) in a mixture of strong acids added to the aqueous coolant [140]. The characteristics of the cerium redox couple in these solutions have been studied [89,141,142]. The radioactive ions can then be recovered from the cerium-containing solution by a process involving electrodialysis and ion-exchange [143], and the adsorption of Ce(IV) complexes has been investigated for this purpose [144], separating it from other lanthanides present in spent nuclear fuels. Ce(III) extraction has been contemplated in nuclear separation processes as PUREX (plutonium and uranium recovery by extraction) [145] and DIAMEX (diamide extraction) [146,147]. Cerium ions and oxides are well-known surrogates for plutonium and other actinide elements.

Radionuclide-contaminated organics can also be treated by cerium MEO. The by-products of dissolution of uranium carbide [148] and ethylenediaminetetraacetic acid (EDTA)-containing solutions from decommissioning processes [149] can be treated, although Ag(II) showed better performance as redox mediator, likely due to the use of nitric acid as solvent. An advantage of Ce(IV), though, is that insoluble precipitates are not formed with chloride ions [150].

### ***Destruction of organics***

Direct electrochemical destruction (oxidation) of organic compounds is seldom performed industrially, as the low solubility of many organics results in low-efficiency processes, while inert anodes such as boron-doped diamond are expensive. MEO is often more appropriate, taking advantage of Ag(II), Fe(III), Co(III) or Ce(IV) the current efficiency of the process of anodically decomposing the organics into CO<sub>2</sub> and water can be increased. Cerium can offer



a cost-effective alternative, having compatibility with chlorides and avoiding the toxicity of cobalt.

One of the first applications for Ce(IV) MEO was the disposal of coal slurries rich in polycyclic aromatic compounds. The oxidation rates were fast [151], and the redox mediator more suitable than Fe(II) [152]. The large scale oxidation of hazardous liquid organic waste with electrogenerated Ce(IV) was patented [153] and developed under the commercial name of CerOx<sup>TM</sup> in the late 1990s [13]. During several years of operation, a pilot-plant with 40 kW capacity produced *ca.* 320 mol h<sup>-1</sup> of Ce(IV). Shown in Figure 13, it was successfully deployed to dispose of dichlorobenzene, xylene, aniline, several alcohols, cyclohexanone, among others, with claimed removal efficiencies of over 99% in most cases [13]. A shortcoming of this technology was the use of nitric acid (rather than milder acids, e.g. MSA), which results in the formation of NO<sub>x</sub> at the electrodes and a requirement of absorber columns to regenerate the electrolyte. It is possible that hydrogen gas evolution at the cathode contributed to high cell potentials and low energy efficiency. Destruction of chemical weapons and explosives by the CerOx<sup>TM</sup> process was considered by the U.S. Army [150] but problems with nitric acid and lack of commercial electrolyzers prompted the adoption of other technologies.

The process explained above and other similar ones can be applied to many waste liquids containing organic compounds, including persistent organic pollutants (POPs). Aniline found in discharges from the dye industry can be completely oxidised to CO<sub>2</sub> by Ce(IV) at Pt and DSA electrodes [154]. The batch oxidation of benzoic acid in sulfuric aqueous solutions for effluent treatment can also be performed [155], although the use of sulfuric acid limited its

removal efficiency to 96% after 456 h. In general, the effect of electrode structure/materials and the development of continuous processes have not been considered.

A Korean-Indian research group has considered applications of cerium MEO for destruction of several organic compounds. The oxidation of phenol has been performed in electrochemical flow cells via Ce(IV) oxidation in nitric acid solutions [156,157], showing nearly 300% increase in efficiency in comparison to direct oxidation. Compared to Ag(II), the cerium mediated process required higher temperatures and showed 5% lower efficiency [158]. Batch destruction of EDTA was also performed in batch and continuous modes, following the concentration decay with a mathematical model [159,160], and its operating conditions studied towards optimization [161,162]. Ideal conditions were found at 95 °C when EDTA and Ce(IV) concentration were 0.07 mol dm<sup>-3</sup> and 0.95 mol dm<sup>-3</sup>, respectively, in 3 mol dm<sup>-3</sup> nitric acid. A modification of the process, coupling ozone and ultrasonication, was found to be highly effective in eliminating phenol, benzoquinone and EDTA [163]. In such configuration ozone can be used to regenerate the Ce(IV) catalyst [164]. The removal of persistent polychlorinated dibenzo-*p*-dioxins and dibenzofurans from fly ash by the process in nitric acid was also assessed [165], showing a removal efficiency of 43%. The removal of methylene blue was much more efficient, 95% oxidized by Ce(IV) after 45 min. in a two-phase batch process [166], with dichloromethane or dichloroethane as the organic phase. Finally, a significant improvement was made compared to the previous works when MSA-based electrolytes were implemented, showing increased destruction efficiency of phenol and avoiding the evolution of NO<sub>x</sub> gases [167], which eliminates the need for gas scrubbers and simplifies the reaction apparatus.

Taiwanese researchers have developed other uses for Ce(IV) MEO, including the removal of acetaminophen from diluted sulfuric acid solutions in an electrochemical flow cell at BDD electrodes [168]. Such electrodes outperformed  $\text{PbO}_2/\text{Sn}_2\text{O}_3\text{-SnO}_2/\text{Ti}$  and Pt. In other work, it was shown that the destruction of polyvinyl alcohol, product of dye and paper industries, in an undivided batch cell is possible in nitric acid solutions [169]. A modified version of the process coupling a cathodic UV photoelectrochemical reaction in a divided cell was also investigated and significantly reduced the specific energy consumption [170]. As previously mentioned, MSA is often a more suitable background electrolyte for electrochemical processes involving cerium. We consider that there are important opportunities for research in the application of MSA electrolytes to organic destruction.

### 6.3 Chemical analysis

Ce(IV) sulfate solutions have an important application in volumetric and potentiometric chemical analysis [171]. Ce(IV) is an oxidizing agent useful for direct titration at room temperature. It is more stable than permanganate and less toxic than the carcinogenic dichromate, giving also fewer by-products. Cerium solutions are clear and, in some cases, the indicator can be omitted after a blank correction. Ammonium cerium(IV) sulphate is commonly used due to its solubility and standardization is usually performed against sodium oxalate by back-titration with Fe(II). Suitable colorimetric redox indicators are [1,10-phenantroline iron (II)] (ferroin) and 2-(phenylamino)benzoic acid (N-phenylanthranilic acid).

Classical volumetric analysis of inorganic compounds such as copper, molybdate, nitrite, persulfate, iron and hydrogen peroxide can be performed with a cerium redox titration [171].

For example, vanadium [172], nitrates [173] and vitamin C (ascorbic acid) [174], can be determined in this way. Potentiometric titration with Ce(IV) is common for Fe(II), Ti(III), As(III), I<sup>-</sup>, hydroquinone and phenols [175] and Ce(IV) is suitable to determine U(IV), updating the standard method using dichromate [176]. Notwithstanding the decline in its use, cerimetry remains as a reliable and relatively inexpensive methodology.

Some spectroscopic methods have taken advantage of Ce(III) ion fluorescence to analyse organic compounds after their oxidation by Ce(IV), e.g. the determination of penicillins [177] and trimeprazine [178]. Chemiluminescence methods enabled by Ce(IV) reduction have been developed for several drugs, including acetaminophen [28], quinine [179], captopril [180], hydrochlorothiazide [181], and chlorpromazine hydrochloride [182]. Reserpine has been determined by UV spectroscopy after its oxidation by Ce(IV) [131]. Due to the availability of standard methods, these techniques have received little attention. New developments could be done in the analysis of highly specialized drugs, enzymes and other organic compounds or the application of these techniques to *in situ* analysis of materials, foodstuffs or tissues.

Volumetric determination of Ce(IV) can be performed with excellent results against a standard solution of Fe(II) prepared with ammonium iron(II) sulphate using ferroin as indicator [183]. If Ce(III) analysis is required, it can be easily oxidised to Ce(IV) by treatment with ammonium persulfate in presence of sulfuric acid and silver nitrate as catalyst [183]. These methods have been used routinely for the determination of cerium in MSA solutions [68,71]. Cerium can also be determined by UV spectroscopy [105,173,184], fluorimetry [185], voltamperometry [173], and potentiometric cells [183]. Atomic absorption

(AA) and inductively coupled plasma mass spectrometry (ICP) are more appropriate techniques for trace analysis.

#### **6.4 Environmental treatment and recycling**

As shown in section 6.2, many hazardous organics can be treated by Ce(IV) MEO and this has been applied to environmental treatment. Pesticide formulations have been removed from solutions with efficiencies of to 99% [186] and the CerOx<sup>TM</sup> process was evaluated by the U.S. Environmental Protection Agency for soil remediation [187]. Since the effluent, slurry or soil to be treated must be diluted in either the electrolyte or separated after use of a dedicated reactor, these methods have limited possibilities for practical use. More suitable process strategies avoid the use of toxic redox mediators or oxidants. In the reuse and treatment of chromium etching solutions containing Cr(IV) from the electronics and colour filter industry, regeneration by Ce(IV) is possible [188,189] but it is highly sensitive to the presence of dichromate impurities.

The need to recycle CeO<sub>2</sub> used in polishing slurries and cerium containing phosphors in lamps has become ever more evident from an environmental and industrial point of view [17,190]. However, the application of classical electrochemical processes to the recovery and recycling of these compounds remains a challenge due to their lack of solubility, which can render chemical digestion, precipitation and extraction more suitable techniques. For instance, acid leaching of CeO<sub>2</sub> polishing slurries in sulfuric acid produces concentrations of 0.02 mol dm<sup>-3</sup> Ce(IV) after 48 h at 125 °C [191]. On the other hand, the recovery of cerium from fluorescent lamps is subordinate to the recovery of yttrium and europium phosphors, which are more valuable [192]. Currently, developed recovery processes involve the removal

of these elements followed by the dissolution of cerium-doped lanthanum phosphate in concentrated sulfuric acid at 120 °C [193], or in a hydrochloric acid - peroxide solution [17].

A form of cerium utilization from aqueous solutions lies actually in the inverse process, i.e. the electrochemical synthesis of CeO<sub>2</sub> nanocrystals and powders [30]. Such materials have applications as catalysts in high temperature fuel cells, catalytic convertors, sensors and anticorrosion coatings [194]. Two methods are currently used [30], the anodic oxidation of Ce(III) and the subsequent formation of the oxide in the bulk solution, or the cathodic generation of a base, which then hydrolyses Ce(IV); pH conditions are crucial. So far, expensive platinum electrodes have been used and the resulting CeO<sub>2</sub> materials are sintered after their preparation. If low current densities are applied, CeO<sub>2</sub> thin films can also be produced [195]. Similar films have been created from chloride solutions and the growth mechanism has been considered as formation of Ce(IV) hydroxide nuclei and posterior growth [196]. Electrophoretic deposition of CeO<sub>2</sub> produces nanostructured coatings as well [197], and their electrodeposition mechanisms have been studied with complexing agents [198]. Composite powders can also be electrochemically produced, for instance CeO<sub>2</sub>-Na-layered silicate [199]. The feasibility of scale-up for these methods remains unclear.

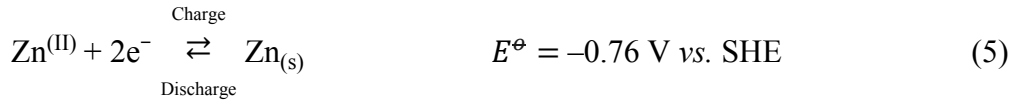
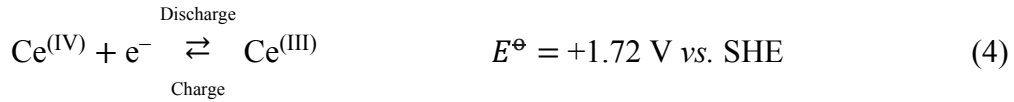
Developing alternative electrochemical recovery methods more effective than precipitation requires more research, although they may be especially useful with dealing with low concentrations of cerium or for the separation of rare earths mixtures. Previously, the separation of Ce(IV) from La(II) and Y(II) in nitric acid solutions was demonstrated by using polyvinyl pyridine anion exchangers for spent nuclear fuels [144]. The oxidation of Ce(III) in rare earth mixtures in nitric acid has also been investigated [200]. The possibility of taking

advantage of electrochemical driven conversion and of the high solubility of cerium (and other lanthanides) in MSA in new applications deserves more research.

## **6.5 Redox flow batteries**

Redox flow batteries (RFBs) are used for medium and large-scale energy storage and consist on two electrolyte compartments separated by an ion-exchange membrane in which reversible electrochemical reactions take place. Their characteristics and applications to the load balancing of a power grid dependent on renewable sources are described elsewhere [201,202]. Several RFB systems have taken advantage of the highly positive standard redox potential of the Ce(III)/Ce(IV) redox couple in order to achieve high cell potential and the resulting increased energy density. These include: divided Zn-Ce [72], undivided Zn-Ce [203], V-Ce [50], modified V-Ce [204], H<sub>2</sub>-Ce (half fuel cell) [205], and Ce concentration cell [206] RFBs. Other, more limited, proposals are a nitroso-R-salt/Fe-Ce system [57] and a diethylenetriaminepentaacetic acid (DTPA)-Ce electrolyte [207]. The main challenges in these systems are parasitic oxygen evolution and the need for cost-effective 3-D electrodes.

The Zn-Ce RFB divided by a proton exchange membrane is currently the most advanced cerium-based battery. It was introduced in 2004 [31] and its characteristics and developments have been recently reviewed [57,72]. This system yields the highest standard cell potential for any aqueous RFB, *ca.* 2.48 V. As shown in Figure 14a, discharge of the battery is based on the reduction of Ce(IV) at the positive electrodes and the oxidation of a zinc deposit at the negative electrode:



Both electrolytes are MSA solutions and a proton exchange membrane separates the positive and negative half-cells. The high solubility of cerium in MSA is critical to realising a high performance Zn-Ce battery. A bipolar arrange of repeated unit flow cells is put together to form a cell stack as a battery module. As in other RFBs, the electrolytes are recirculated with the aid of pumps between the tanks and the reactors. Currently, platinized titanium mesh electrodes are required to minimize potential losses at high current densities and avoid material corrosion [68]. Although carbon felt (widely used in other RFBs) can increase current output and voltage efficiency, carbon-based materials are easily corroded [71]. Catalyst-modified carbon felts or foams (e.g. [95-97]) could greatly improve the performance of the battery and lower its cost, provided an effective connection to the bipolar electrodes.

In an early pilot Zn-Ce RFB using planar Pt-Ti/Ti bipolar electrodes (projected area 0.24 m<sup>2</sup>) and operating at 50 mA cm<sup>-2</sup> and 60 °C, coulombic, voltage and energy efficiencies up to 90%, 64% and 55% were achieved over 25 charge-discharge cycles, respectively [72]. Volumes of 288 dm<sup>3</sup> of the positive and negative electrolytes were used, having a composition of 0.6 mol dm<sup>-3</sup> Ce(III) and 1.0 mol dm<sup>-3</sup> Zn(II) in 3.5 mol dm<sup>-3</sup> MSA, and the negative of 0.4 mol dm<sup>-3</sup> Ce(III) and 1.5 mol dm<sup>-3</sup> Zn(II) in 2.7 mol dm<sup>-3</sup> MSA.



Leung *et al.* have described a laboratory Zn-Ce cell showing the effect of electrode materials and electrolyte compositions [68,94]. Charge density increases with higher concentration of Ce(III), although a maximum of  $0.8 \text{ mol dm}^{-3}$  Ce(III) is employed in order to avoid the precipitation of Ce(IV), which has lower solubility. In terms of electrode materials, only 3D structures such as Pt-Ti mesh and graphite felt were able to maintain a practical combination of cell potential and discharge current density (Figure 15). Under optimal conditions using Pt-Ti mesh electrodes, the cell showed a charge efficiency of 99.4% and an energy efficiency of 59.3%. The electrolytes were  $0.8 \text{ mol dm}^{-3}$  Ce(III) in  $4.0 \text{ mol dm}^{-3}$  MSA for the positive half-cell and  $1.5 \text{ mol dm}^{-3}$  Zn(II) in  $1.0 \text{ mol dm}^{-3}$  MSA for the negative half-cell. The corresponding charge-discharge cycles are shown in Figure 16.

Nikiforidis *et al.* characterized and evaluated a number of Pt and Pt/Ir materials as the positive electrode of the battery [71]. Electrochemical surface area, cyclic voltammetry and the determination of exchange current densities revealed that Pt/Ir materials had the highest electrocatalytic activity and that higher reaction rates would be achieved at a temperature of  $60^\circ\text{C}$ . Planar carbon composites studied in the same work degraded rapidly. The same authors studied the cycling performance of the same electrodes [66]. At a rotating disc electrode, a higher mass transport via improved electrolyte flow increased the current efficiency during the cycle. It was also found that the electrodes lost some of their activity after 150-200 charge-discharge cycles. Charge efficiencies over 90% and energy efficiencies above 60% were achieved at low current densities of  $10 \text{ mA cm}^{-2}$ , using electrolytes containing  $0.6 \text{ Ce(IV) mol dm}^{-3}$  in  $3.5 \text{ mol dm}^{-3}$  MSA and  $2.5 \text{ mol dm}^{-3}$  of Zn(II)  $\text{mol dm}^{-3}$  in  $1.5 \text{ mol dm}^{-3}$  MSA [208].

Following fundamental studies of the Ce(III)/Ce(IV) couple in MSA [56], Xie *et al.* reported an increase in the solubility of cerium and improved reversibility of the redox reaction when employing a sulfuric acid/MSA positive electrolyte [57,79]. The reaction was studied by voltamperometry and chronoamperometry at Pt electrodes in order to estimate the exchange current density and standard rate constant using different mixture ratios [79]. A coulombic efficiency of 87.3% and an energy efficiency of 73.5% in a flow cell with a positive electrolyte composition of 1.0 mol dm<sup>-3</sup> Ce(III) in a mixture of 2.0 mol dm<sup>-3</sup> MSA and 0.5 mol dm<sup>-3</sup> sulfuric acid. Additives for the positive electrolyte such as sulfosalicylic [86] and sulfamic acid [87] were also studied, showing moderate improvements on the kinetics of the reaction.

Nikiforidis *et al.* showed that the exchange current density and the diffusion coefficients of cerium ions can increase significantly in mixtures of MSA and hydrochloric, nitric and sulfuric acid in adequate proportions; the solution resistivity and electron charge-transfer resistance also decreasing [81]. Although the addition of 0.5 mol dm<sup>-3</sup> hydrochloric acid gave rise to the fastest reaction kinetics, long-term pitting corrosion of the Pt-Ti electrodes may be a problem. Mixtures of 3 mol dm<sup>-3</sup> MSA and 1 mol dm<sup>-3</sup> sulfuric acid seem more appropriate for the Zn-Ce RFB.

The cell potential of the Zn-Ce system has been modelled for an ideal unit flow cell [209]. The thermodynamic, kinetic and ohmic cell potential components were quantified in the relationship between cell potential and current density. The open circuit cell potential varies from ca. 2.35 V to 2.47 V when the battery goes from a state of charge of 10% to 90%. Electrolytes with low conductivity produce higher ohmic drops, especially when the

electrode-membrane gaps are  $> 5\text{mm}$ . Operation at low current density (e.g. when using a 3-D electrode) reduces the potential losses significantly. The effects of the oxygen evolution have yet to be considered in the modelling of electrodes for cerium regeneration.

Currently, the main challenges of this system are the material composition of bipolar plates, the corrosion of the (desirable) carbon felt-bipolar electrode interphase, progressive self-discharge of the negative half-cell (acid conditions promote zinc dissolution via hydrogen evolution), and a cerium concentration limited to  $0.8\text{ mol dm}^{-3}$ . Hydrogen ( $E_{\text{H}/\text{H}^+}^{\ominus} = 0\text{ V vs. SHE}$ ) and oxygen ( $E_{\text{O}_2/\text{OH}^-}^{\ominus} = +1.23\text{ V vs. SHE}$ ) evolution reactions take place at the negative and positive electrodes, respectively, as secondary reactions. Appropriate selection of acid concentration, overpotential, electrode geometry/material and electrolyte flow rate could significantly improve the performance of the system.

An undivided variant of the Zn-Ce cell, shown in Figure 14b, has also been studied [203,210]. Both positive and negative active species are present in a single electrolyte. An ion-permeable membrane is avoided and only one electrolyte flow circuit is required. Potentially, such systems can greatly reduce the overall cost of a RFB. In this RFB, the concentration of MSA was kept under  $0.5\text{ mol dm}^{-3}$  in order to avoid hydrogen evolution at the negative electrode, meaning that the concentration of cerium was limited to  $0.2\text{ mol dm}^{-3}$  [210], and the battery showed an energy efficiency of 72% due to an increased oxygen evolution reaction. Alternative electrolyte compositions and the use of additives or complexing agents are some of the strategies that could marginally improve the efficiency and energy density of this RFB.

### ***The V-Ce RFB***

A V-Ce RFB, shown in Figure 14c, has been proposed as an attempt to avoid the control of zinc electrodeposition needed at the negative electrode of the Zn-Ce system. In its first version based on sulfuric acid electrolytes an open circuit cell potential of 1.9 V was measured with a current efficiency up to 89% [50], and voltammetry studies showed that platinum oxide can affect the rate of the cerium reaction [75]. The main drawback of this battery is electrolyte cross-mixing and, as a result, anionic ion exchange membranes have been tested in place of cationic Nafion, proving less permeable to the active species [211]. The stability of anionic membranes is usually limited and the degrading effect of the oxidant Ce(IV) has not been addressed by long-term studies. The V-Ce system has been demonstrated with a zero-gap architecture and serpentine flow fields [212], where the MSA-based electrolytes allowed to use higher concentration of cerium. A V-Ce RFB could, in principle, be applied to hydrogen production by chemically discharging the vanadium electrolyte with a Mo<sub>2</sub>C catalyst [204].

### ***Other Ce-based RFBs***

In principle, a simple Ce-Ce concentration cell can be used as an RFB as considered in a patent application [206] and a book by R. Zito [213]. In practice, the need to establish and maintain a large concentration gradient over the membrane restricts practical developments and requires high quality cell division as well as high surface area electrodes. A H<sub>2</sub>-Ce fuel cell has been considered in order to increase the operational current density and power output while avoid the limitations set by zinc deposition and cross-mixing [205]. Membrane permeability towards the gas half-cell becomes critical. The addition of nitroso-R-salt or the

Fe(II)/Fe(III) redox couple has been suggested as a way to increase the energy density of the cerium electrolyte in the Zn-Ce battery [57] but this could carry stability and by-product issues in the positive electrolyte. An electrolyte based on diethylenetriaminepentaacetic acid (DTPA)-Ce showed high reversibility [207], but its stability depends on keeping a near neutral pH. A dual process involving the anodic generation of Ce(IV) at the positive electrodes and Ti(III) at the negative electrode was proposed for the reduction of organics [214]. This concept was not further developed but it could potentially be transformed into a MSA-based RFB with a maximum standard cell potential of 1.7 V.

## 6.6. Gas scrubbing

The electrochemical removal of noxious substances from gases can also be performed. For instance, purification of air from inorganic, organic and biological compounds is possible in gas scrubbers using Ce(IV) [27]. Lapicque *et al.* proposed an SO<sub>2</sub> and NO<sub>x</sub> scrubbing system based on the absorption of these gases by an aqueous medium and its further oxidation by Ce(IV), obtaining sulfuric and nitric acid as by-products [215,216]. Electrode kinetics for the regeneration of the oxidant at a filter-press cell with platinum electrodes were determined [77]. The rate constant and time of NO<sub>x</sub> degradation, mainly via the oxidation of nitrous acid to nitric acid, were studied and simulated for the pilot process [173]. The conversion was fast in 0.5 mol dm<sup>-3</sup> sulfuric acid solutions, higher concentrations yielding lower rates. The degradation of SO<sub>2</sub> was investigated in a similar way [217], revealing that oxidation to dithionate reduces the conversion efficiency, a sulfuric acid concentration of 5.0 mol dm<sup>-3</sup> minimized this secondary reaction. The pilot-scale operation, shown in Figure 17, was performed and optimized for the simultaneous removal both gases [218], showing removal efficiencies of SO<sub>2</sub> and NO<sub>x</sub> of 100% and 45%, respectively.

In related work, H<sub>2</sub>S removal efficiencies of more than 95% from a scrubber feed with the oxidant from a flow cell reached using 0.8 mol dm<sup>-3</sup> Ce(IV) solutions [219]. The authors highlighted several advantages over other electrochemical methods for H<sub>2</sub>S removal involving molten electrolytes and high temperatures, e.g. [220]. Another possibility is the oxidation of bromine, the kinetics of this reaction being available [221].

## 6.7. Other applications

The anodic generation of Ce(IV) paired to other useful electrochemical cathodic reactions is possible. For instance, simultaneous production of copper powder [222], ethylene glycol [223], and Ti(III) for the reduction of organics [214] have been proposed as complementary processes in filter-press reactors. Oxidation of water has importance in the field of photochemical water splitting and the role of cerium as oxidant via a RuO<sub>2</sub> catalyst has received some consideration [224-226], and a similar work on the evolution of Cl<sub>2</sub> from chloride ions is available [227,228]. The Ce(III)/Ce(IV) redox couple also participates in the Belousov-Zhabotinsky oscillating reaction via autocatalytic oxidation [229,230]. Efforts have been devoted to further study the effects and kinetics of cerium in such complex reaction mechanisms [231-235], including the reaction mechanism with malonic acid [236,237].

## 7. Summary

1. Ce(IV) ions in acid electrolyte, which can be readily generated by anodic oxidation of Ce(III) ions, provide a highly oxidising species.
2. Common supporting electrolytes include aqueous sulphuric, nitric and methanesulfonic acids, the last being favoured when high cerium concentrations are involved. Complex

interactions between Ce and the ligands present, can significantly affect cerium redox kinetics.

3. Rapid kinetics of Ce(IV) reduction and Ce(III) oxidation have normally utilised platinum or iridium surfaces. 3-D carbon electrodes can prove successful although the grade electrical connection method is critical. For technological applications, dispersed precious metals, such as platinum, on inert substrates such as titanium (or occasionally vitreous carbon), have become increasingly popular electrocatalysts.
4. Classical uses of soluble cerium (IV) ions in acidic media have been found in redox titrations, mediated electrosynthesis and specialised cleaning such as nuclear decontamination. The first two have often deployed sulphuric acid media while the last generally involves nitric acid. A growing trend over the last 30 years has been the use of methanesulfonic acid in mediated organic electrosynthesis.
5. More recently, cerium redox half-cells have found use in redox flow batteries, including Zn-Ce and V-Ce types, where the use of high cerium concentrations in methanesulfonic acid enables a high volumetric energy density.
6. In view of their importance to scale-up and industrial processing, it is unfortunate that few studies have considered critical aspects of cerium redox electrochemistry such as electrode form, electrocatalyst structure, active electrode area and choice of indifferent electrolyte.

## **8. Future developments**

Several developing research areas deserve attention.

- New electrogenerated cerium mediated organic synthesis are possible, e.g., application to the many ammonium hexanitrate-cerium(IV) mediated reactions found in the organic literature.

- Development of cerium cleaning and recovery solutions taking advantage of aqueous MSA as a supporting electrolyte.
- The challenge of enabling the use of carbon-based 3-D electrodes by an improved method of electrical connection to bipolar electrodes or current feeders.
- Development of cerium polyoxometalates (which have been studied as artificial proteases) in the search for higher solubility and better electrochemical reversibility, particularly in redox flow batteries.
- The urgent need for cleaner methods for cerium (and other rare earth) extraction and recycling, as these metals tend to have a severe environmental impact.
- The possible use of supercritical solvents for extraction of organic products in mediated electrosynthesis.
- Electrode materials able to resist very positive potential values in the presence of the Ce(IV) oxidant with minimal corrosion and facile scale-up.

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**Table 1. Standard redox potentials involving lanthanide elements as dissolved species**  
[38].

Element	Atomic number	Atomic mass	Redox couple	Standard electrode potential vs. SHE / V
Cerium	58	140.116	$\text{Ce}^{4+}/\text{Ce}^{3+}$	+1.74
Praseodymium	59	140.908	$\text{Pr}^{4+}/\text{Pr}^{3+}$	+3.2
Neodymium	60	144.24	$\text{Nd}^{4+}/\text{Nd}^{3+}$	+5.0
Samarium	62	150.36	$\text{Sm}^{3+}/\text{Sm}^{2+}$	−1.55
Europium	63	151.964	$\text{Eu}^{3+}/\text{Eu}^{2+}$	−0.35
Terbium	65	158.925	$\text{Tb}^{4+}/\text{Tb}^{3+}$	+3.1
Dysprosium	66	162.5	$\text{Dy}^{4+}/\text{Dy}^{3+}$	+5.2
Thulium	69	168.934	$\text{Tm}^{3+}/\text{Tm}^{2+}$	−2.3
Ytterbium	70	173.04	$\text{Yb}^{3+}/\text{Yb}^{2+}$	−1.15

**Table 2. Standard and formal electrode potentials for the Ce(III)/Ce(IV) redox couple.**

Reaction	Supporting electrolyte	Electrode potential vs. SHE / V	Reference
$\text{Ce}^{(\text{IV})} + \text{e}^- \rightleftharpoons \text{Ce}^{(\text{III})}$	1 mol dm <sup>-3</sup> HClO <sub>4</sub>	+1.74	[55]
	1 mol dm <sup>-3</sup> HNO <sub>3</sub>	+1.61	[55]
	1 mol dm <sup>-3</sup> H <sub>2</sub> SO <sub>4</sub>	+1.44	[55]
	1 mol dm <sup>-3</sup> HCl	+1.28	[55]
	1 mol dm <sup>-3</sup> MSA	+1.61	[56]
$\text{Ce}^{3+} + 3\text{e}^- \rightleftharpoons \text{Ce}_{(\text{s})}$		-2.48	[55]

**Table 3. Selected voltammetric studies for the Ce(III)/Ce(IV) redox couple on inert substrates. After [72].**

Author	Electrode material	Electrolyte composition / mol dm <sup>-3</sup>	Method of determination	Temperature (T) / °C	Electron transfer coefficient ( $\alpha$ )	Formal potential, ( $E^0_e$ ) / V	Diffusion coefficient Ce(IV) (D) / cm <sup>2</sup> s <sup>-1</sup>	Diffusion coefficient Ce(III) (D) / cm <sup>2</sup> s <sup>-1</sup>	Reaction rate constant ( $k_s$ ) / cm s <sup>-1</sup>	Reference
Bishop et al. (1981)	Pt	0.5 H <sub>2</sub> SO <sub>4</sub> 0.02 Ce(III)	RDE	20	0.30 (anod.)	1.22 vs. SCE	NG	NG	3.5×10 <sup>-5</sup>	[64]
	Au	0.5 H <sub>2</sub> SO <sub>4</sub> 0.02 Ce(III)			0.16(anod.)	1.12 vs. SCE			7.3×10 <sup>-5</sup>	
	GC	0.5 H <sub>2</sub> SO <sub>4</sub> 0.02 Ce(III)			0.49(anod.)	1.23 vs. SCE			8.7×10 <sup>-5</sup>	
Bonewitz et al. (1970)	Au	1 H <sub>2</sub> SO <sub>4</sub> 0.01 Ce(III) 0.01 Ce(IV)	LSV	RT	0.65(anod.)	1.35–1.50 vs. SHE	NG	NG	4.0×10 <sup>-4</sup>	[73]
Fang et al. (2002)	GC	0.1 H <sub>2</sub> SO <sub>4</sub> 0.01 Ce(III)	CV	25	NG	1.21 vs. Ag/AgCl	NG	NG	NG	[50]
Galus et al. (1963)	Pt	0.5 H <sub>2</sub> SO <sub>4</sub> 0.01 Ce(IV)	RDE	25	0.21(cath.)	NG	NG	NG	3.7×10 <sup>-4</sup>	[22]
	CP				0.28(cath.)				3.8×10 <sup>-4</sup>	
Greef et al. (1968)	Pt	1 H <sub>2</sub> SO <sub>4</sub> 1×10 <sup>-4</sup> Ce(III) 0.001 Ce(IV)	RDE	22±1	0.3	NG	3.4×10 <sup>-6</sup>	NG	NG	[74]
Kiekens et al. (1981)	Au	1 H <sub>2</sub> SO <sub>4</sub> 0.001 Ce(III)	RDE	20±0.1	0.33(cath.)	NG	3.4×10 <sup>-6</sup>	NG	2.0×10 <sup>-4</sup>	[63]
	GC	0.010 Ce(IV)			0.25(cath.)		3.7×10 <sup>-6</sup>		3.2×10 <sup>-4</sup>	
	Ir				0.26(cath.)		3.7×10 <sup>-6</sup>		3.9×10 <sup>-4</sup>	
Kuhn et al. (1985)	Pt	0.5 H <sub>2</sub> SO <sub>4</sub> 0.012 Ce(IV) 0.16 Ce(III)	RDE	25	0.2 (cath.) 0.4–0.6 (anod.)	NG	NG	NG	3.7 × 10 <sup>-4</sup>	[61]
Liu et al. (2004)	Pt	1.25 H <sub>2</sub> SO <sub>4</sub> 0.4 Ce(IV)	CV	25	0.132 (cath.)	0.68 vs. MSRE	NG	NG	4.1×10 <sup>-4</sup>	[75]
Maeda et al. (1999)	BDD	0.1 H <sub>2</sub> SO <sub>4</sub> 0.006 Ce(III)	CV	25	0.28 (anod.)	1.19 vs. SCE	NG	1.05×10 <sup>-5</sup>	2.0×10 <sup>-6</sup>	[76]
		0.1 HNO <sub>3</sub> 0.006 Ce(III)			0.27 (anod.)	1.40 vs. SCE		0.55×10 <sup>-5</sup>	1.4×10 <sup>-5</sup>	
Nzikou et al. (1995)	Pt	0.1–5.0 H <sub>2</sub> SO <sub>4</sub> 0.02 Ce(III) 0.01 Ce(IV)	LSV	25±0.2	0.29 (anod.)	0.77 vs. MSRE	4.5–1.5×10 <sup>-6</sup>	4.8–2.1×10 <sup>-6</sup>	3.8×10 <sup>-4</sup> (anod.)	[77]
			RDE		0.31 (cath.)				5.0×10 <sup>-5</sup> (cath.)	
Pletcher et al. (1988)	GC	5 HNO <sub>3</sub> 0.030 Ce(III)	CV	18	NG	1.45 vs. SCE	NG	6.2±0.3 ×10 <sup>-6</sup>	3.3±0.7 ×10 <sup>-2</sup>	[59]
Randle et al. (1983)	Pt	0.5 H <sub>2</sub> SO <sub>4</sub> 0.058 Ce(III) 0.007 Ce(IV)	RDE	25	0.59 (anod.)	NG	NG	5.2±0.3 ×10 <sup>-6</sup>	3.5×10 <sup>-5</sup>	[60]
Sacchetto et al. (1992)	Pt	0.5 H <sub>2</sub> SO <sub>4</sub> 0.018 Ce(III)	RDE	NG	0.28(cath.)	1.17 vs. SCE	NG	NG	6.3×10 <sup>-4</sup> (cath.)	[78]
					0.34 (anod.)				11.3×10 <sup>-4</sup> (anod.)	
	Au	0.5 H <sub>2</sub> SO <sub>4</sub> 0.018 Ce(III) 0.018 Ce(IV)			0.19(cath.) 0.12(anod.)	1.17 vs. SHE			21.0×10 <sup>-4</sup> (cath.) 14.2×10 <sup>-4</sup> (anod.)	

Abbreviations: CA for chronoamperometry, GC for glassy carbon, Gr for graphite, CV for cyclic voltammetry, LSV for linear sweep voltammetry, NG for not given, RDE for rotating disc electrode.

**Table 4. Selected voltammetric studies of the Ce(III)/Ce(IV) redox couple in reported or proposed electrolytes for Zn-Ce RFBs. After [72].**

Author	Electrode material	Electrolyte composition mol dm <sup>-3</sup>	Method of determination	Temperature (T) / °C	Diffusion coefficient Ce(IV) (D) / cm <sup>2</sup> s <sup>-1</sup>	Diffusion coefficient Ce(III) (D) / cm <sup>2</sup> s <sup>-1</sup>	Reaction rate constant (k <sub>s</sub> ) / cm s <sup>-1</sup>	Exchange current density (j <sup>0</sup> ) / A cm <sup>-2</sup>	Reference
Devadoss et al. (2008)	GC	1.0 MSA 0.152 Ce(III)	CV	25±1	NG	0.69×10 <sup>-6</sup>	1.65×10 <sup>-3</sup>	NG	[84]
Leung et al. (2011)	Pt	4.0 MSA 0.8 Ce(III)	CV	22 50	NG	0.5×10 <sup>-6</sup> 1.52×10 <sup>-6</sup>	NG	NG	[68]
Modiba et al. (2012)	Pt	1 H <sub>2</sub> SO <sub>4</sub> 0.1 Ce(IV) 1 H <sub>2</sub> SO <sub>4</sub> 0.1 Ce(IV) 0.03 EDTA 1 H <sub>2</sub> SO <sub>4</sub> 0.1 Ce(IV) 0.03 DTPA 0.1 Ce(IV)	CV EIS	RT	2.4×10 <sup>-6</sup> 1.3×10 <sup>-6</sup> 1.1×10 <sup>-6</sup>	NG	1.6×10 <sup>-4</sup> 1.9×10 <sup>-4</sup> 3.1×10 <sup>-4</sup>	NG	[85]
Nikiforidis et al. (2014)	Pt	4.5 MSA 0.8 Ce(III) 4.5 MSA 0.2 Ce(IV) 0.02 Ce(III) 3.1 MSA 0.59 Ce(IV) 0.07 Ce(III) 0.7 Zn(II)	CV LSV EIS RDE	25 60 25 60	4.63×10 <sup>-7</sup> 1.32×10 <sup>-7</sup> NG 2.17×10 <sup>-7</sup> 4.17×10 <sup>-7</sup>	NG	NG 1.16×10 <sup>-3</sup> 3.42×10 <sup>-3</sup>	NG 0.37 (Tafel) 0.24 (EIS) NG	[71]
Xie et al. (2011)a	Pt	2 MSA 0.2 Ce(III) 0.2 Ce(IV) 2 MSA 0.75 H <sub>2</sub> SO <sub>4</sub> 0.2 Ce(III) 0.2 Ce(IV)	LSV RDE CA	25	2.68×10 <sup>-6</sup> (RDE) 2.56×10 <sup>-6</sup> (CA) 5.93×10 <sup>-6</sup> (RDE) 5.87×10 <sup>-6</sup> (CA)	NG	0.79×10 <sup>-4</sup> 1.48×10 <sup>-4</sup>	1.53×10 <sup>-3</sup> 2.86×10 <sup>-3</sup>	[79]
	Gr	1 MSA 1 H <sub>2</sub> SO <sub>4</sub> 0.2 Ce(III) 0.2 Ce(IV)			NG		4.17×10 <sup>-4</sup>	8.05×10 <sup>-3</sup>	
Xie et al. (2011)b	Gr	2 MSA 0.2 Ce(III) 0.2 Ce(IV)	CA RDE CV	25	2.56×10 <sup>-6</sup> (CA) 2.68×10 <sup>-6</sup> (RDE)	5.37×10 <sup>-6</sup> (CA) 5.56×10 <sup>-6</sup> (RDE)	4.06×10 <sup>-4</sup>	9.8×10 <sup>-3</sup>	[56]

Author	Electrode material	Electrolyte composition mol dm <sup>-3</sup>	Method of determination	Temperature ( <i>T</i> ) / °C	Diffusion coefficient Ce(IV) ( <i>D</i> ) / cm <sup>2</sup> s <sup>-1</sup>	Diffusion coefficient Ce(III) ( <i>D</i> ) / cm <sup>2</sup> s <sup>-1</sup>	Reaction rate constant ( <i>k<sub>s</sub></i> ) / cm s <sup>-1</sup>	Exchange current density ( <i>j<sup>0</sup></i> ) / A cm <sup>-2</sup>	Reference
Xie et al. (2011)c	Pt	1 H <sub>2</sub> SO <sub>4</sub> 0.005 Ce(III) 0.005 Ce(IV) 0.005 SSA	CV RDE	NG	NG	6.5×10 <sup>-6</sup>	3.2×10 <sup>-4</sup>	NG	[86]
Xiong et al. (2012)	Pt	1 NH <sub>2</sub> SO <sub>3</sub> H 0.3 Ce(III) 0.1 Ce(IV)	CV	30	NG	5.93×10 <sup>-6</sup>	4.95×10 <sup>-5</sup>	5.95×10 <sup>-4</sup>	[87]

Abbreviations: CA for chronoamperometry, GC for glassy carbon, Gr for graphite, CV for cyclic voltammetry, LSV for linear sweep voltammetry, NG for not given, RDE for rotating disc electrode.



## Figure captions

**Figure 1.** The Ce(III)/Ce(IV) redox reaction, its applications and major driving factors.

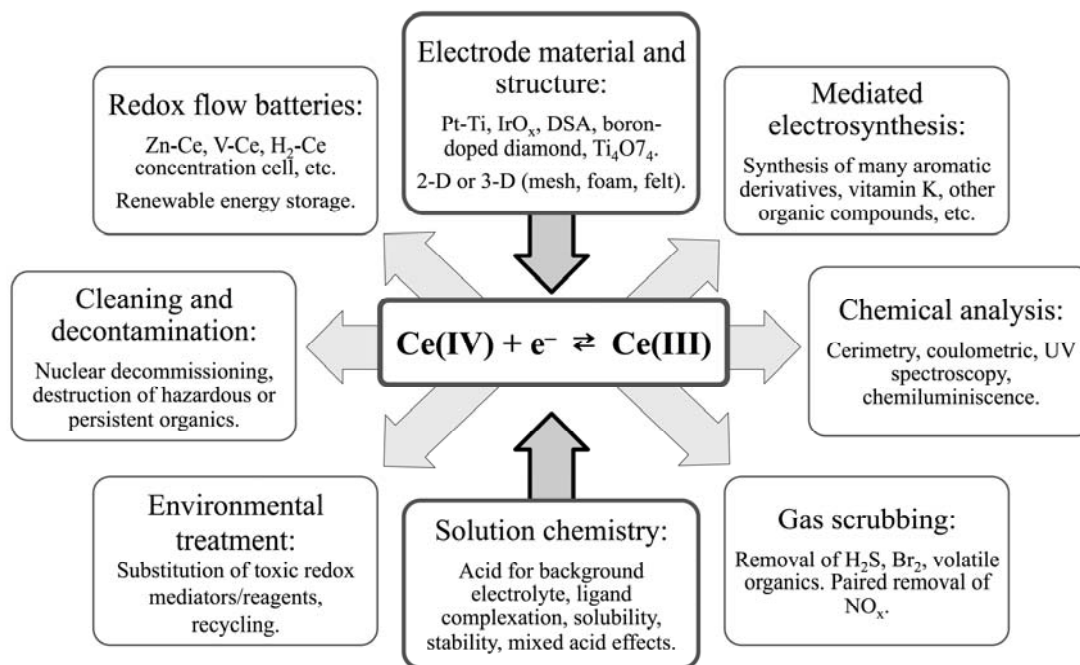
**Figure 2.** Developments in soluble cerium ion chemistry and their applications.

Titration of iron and hexacyanoferrate	1861	[18]
Aniline black mordant, oxidation of dyestuffs	1900s	[19]
Introduction of cerimetry using colorimetric indicators	1928	[18]
Coulometric analysis of iron	1951	[20]
Electrochemical study of redox potential and kinetics	1951	[21]
Study of reaction kinetics using rotating disc electrode	1963	[22]
Electrogeneration of Ce(IV) for mediated synthesis	1968	[23]
Patent for destruction of organics	1972	[24]
Patent for nuclear decontamination cleaning solutions	1980	[25]
MSA-based electrolytes for mediated electrosynthesis	1987	[26]
Patent for electrochemical gas scrubbing	1988	[27]
Chemiluminescence determination of drugs	1989	[28]
Mediated electrosynthesis of tetrahydroanthraquinone	1993	[29]
Electrosynthesis of nanocrystalline cerium oxide	1995	[30]
Large-scale process for toxic waste destruction	1998	[13]
Zinc-cerium redox flow battery	2004	[31]
Mediated electrosynthesis of vitamin K <sub>3</sub>	2007	[32]
Mass transport study of 3-D electrodes in flow cells	2016	[33]

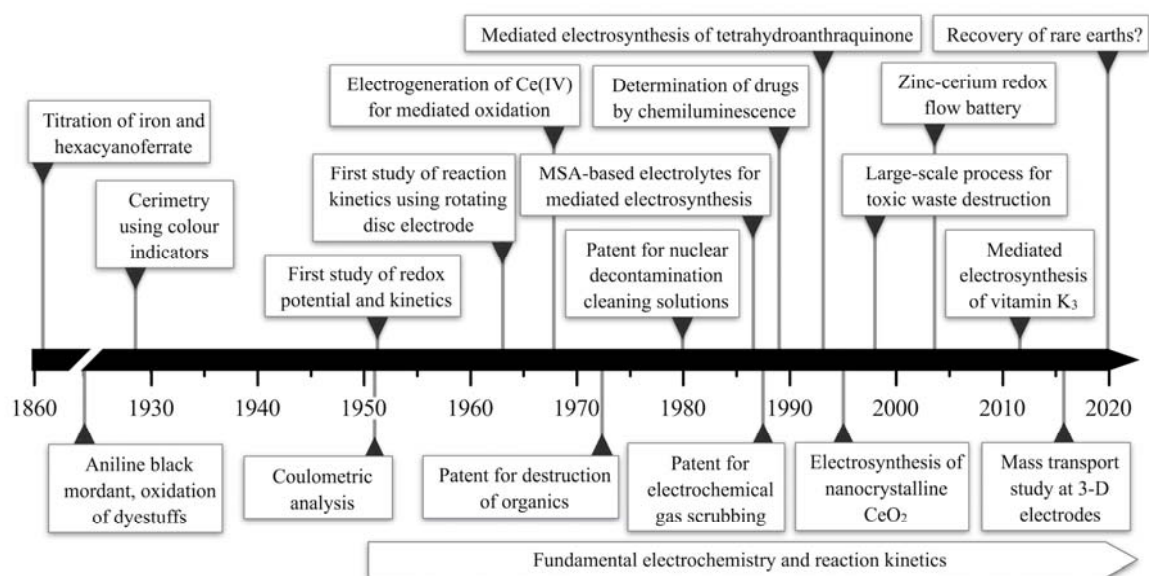
- Figure 3.** Equilibrium potential-pH speciation diagram for cerium in water at 25 °C. After Pourbaix [35].
- Figure 4.** The solubility of cerium ions in methanesulfonic acid (MSA). After Spotnitz *et al.* [34].
- Figure 5.** The speciation of cerium ion complexes in sulfuric acid [50].
- Figure 6.** Schematic protonation and transforming of conformation of Ce(IV) complex ions during an electrode reaction. After Xie *et al.* [57].
- Figure 7.** Cyclic voltammetry in a solution of 0.8 mol dm<sup>-3</sup> Ce(III) at a Pt electrode, showing the effect of free MSA concentration on cerium oxidation at 25 °C, potential scan rate: 0.2 V s<sup>-1</sup> [33].
- Figure 8.** a) Linear sweep voltammetry showing cerium (IV) ion reduction at platinum electrodes at different rotation rates; b) Levich plot relating limiting current and rotation rate. Electrolyte containing 0.4 mol dm<sup>-3</sup> Ce(IV) and 0.4 mol dm<sup>-3</sup> Ce(III) in 4.0 mol dm<sup>-3</sup> MSA at 25 °C, potential scan rate: 0.05 V s<sup>-1</sup> [33].
- Figure 9.** SEM images of 2-D and 3-D platinized titanium electrodes: a) Pt-Ti plate, b) Pt-Ti mesh and c) Pt-Ti micromesh.
- Figure 10.** Process flow diagram for the cerium mediated electrosynthesis of tetrahydroanthraquinone [11].
- Figure 11.** Cerium mediated electrosynthesis of tetrahydroanthraquinone, showing a) production of naphthoquinone and b) production of tetrahydroanthraquinone. After Harrison and Théorêt [11].
- Figure 12.** Cerium mediated electrosynthesis of vitamin K<sub>3</sub>.
- Figure 13.** Process flow diagram for the CerOx<sup>TM</sup> process for destruction of organics. After Varela *et al.* [13].

- Figure 14.** Cerium-based redox flow batteries: a) divided Zn-Ce RFB, b) undivided Zn-Ce RFB, c) V-Ce RFB.
- Figure 15.** Performance of different positive electrode materials for the Zn-Ce redox flow battery, as indicated by the achieved cell potential with increasing current density at 50 °C [94]. Mean linear electrolyte flow velocity: 3.9 cm s<sup>-1</sup>.
- Figure 16.** Life cycle of a zinc–cerium battery charging at 50 mA cm<sup>-2</sup> for 3 h followed by 15 min charge/discharge cycles at 50 °C. Mean linear electrolyte flow velocity: 3.9 cm s<sup>-1</sup>. After Leung *et al.* [94].
- Figure 17.** Process flow diagram for the continuous treatment of SO<sub>2</sub>/NO<sub>x</sub>-containing air. After Hoffmann *et al.* [218].

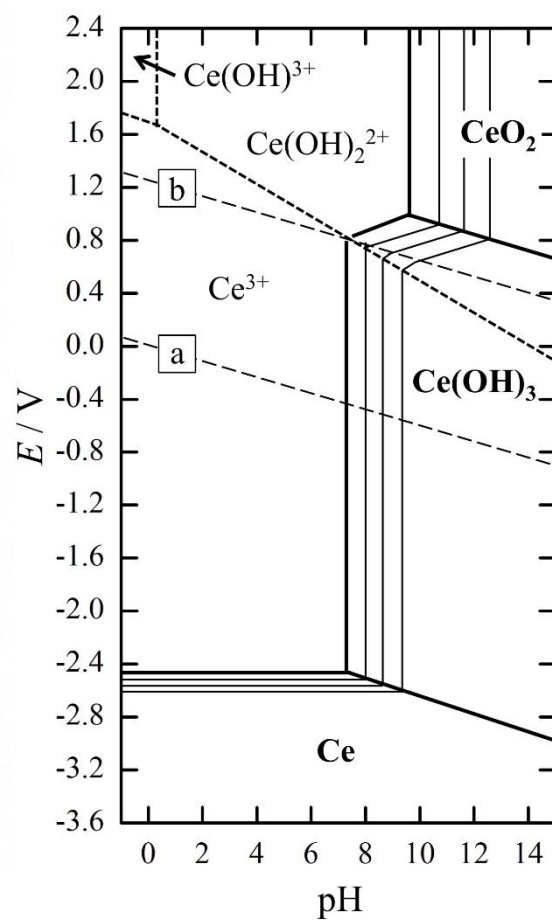
## Figures



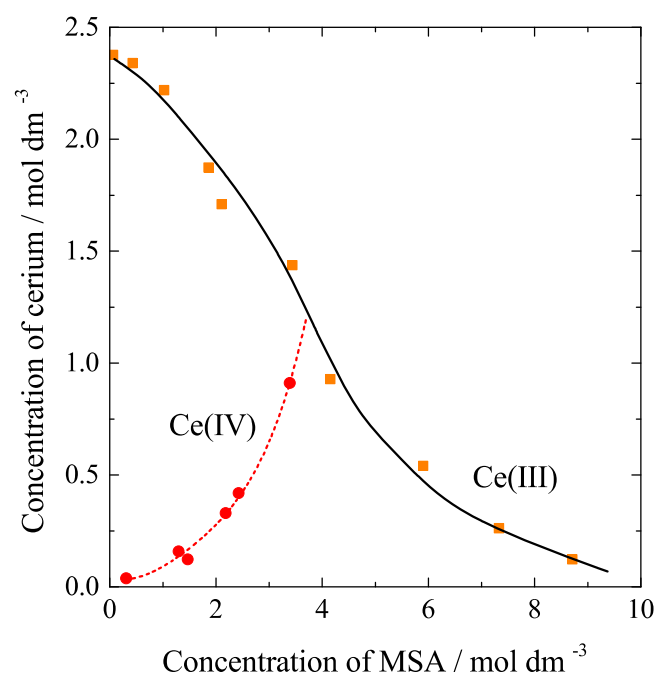
**Figure 1.**



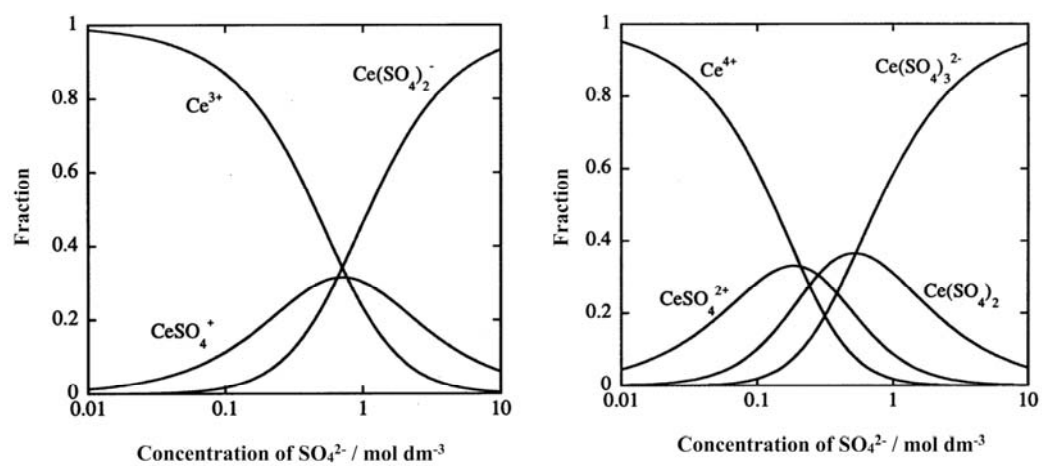
**Figure 2.**



**Figure 3.**

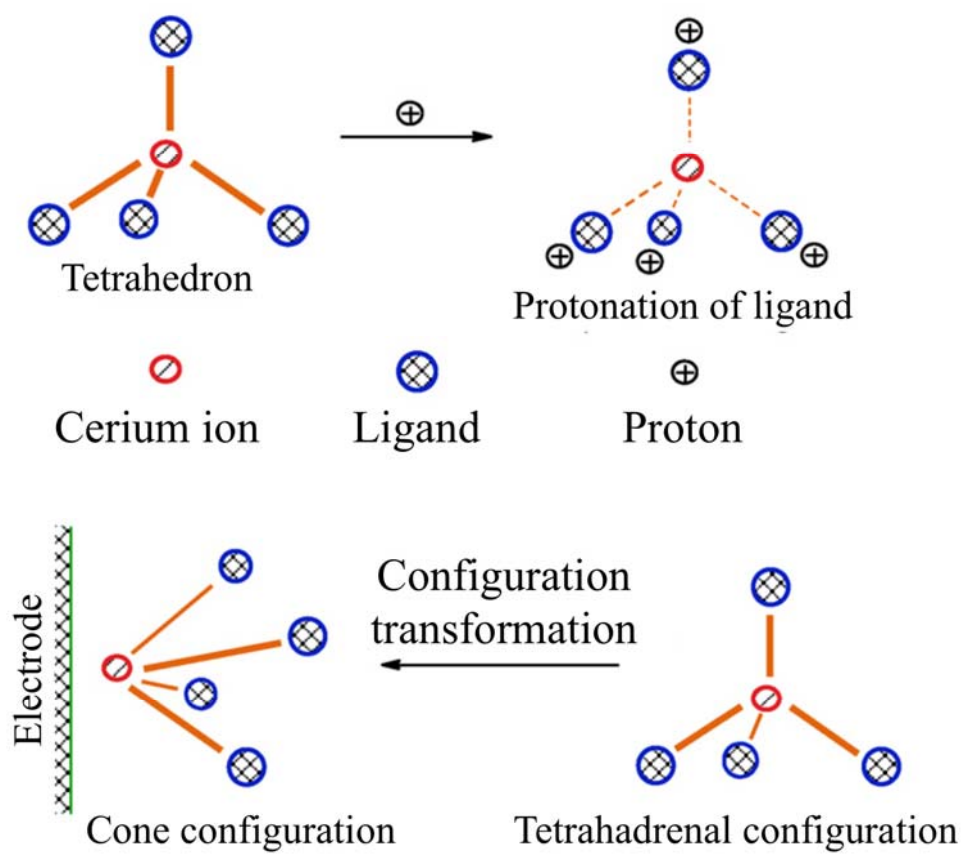


**Figure 4.**

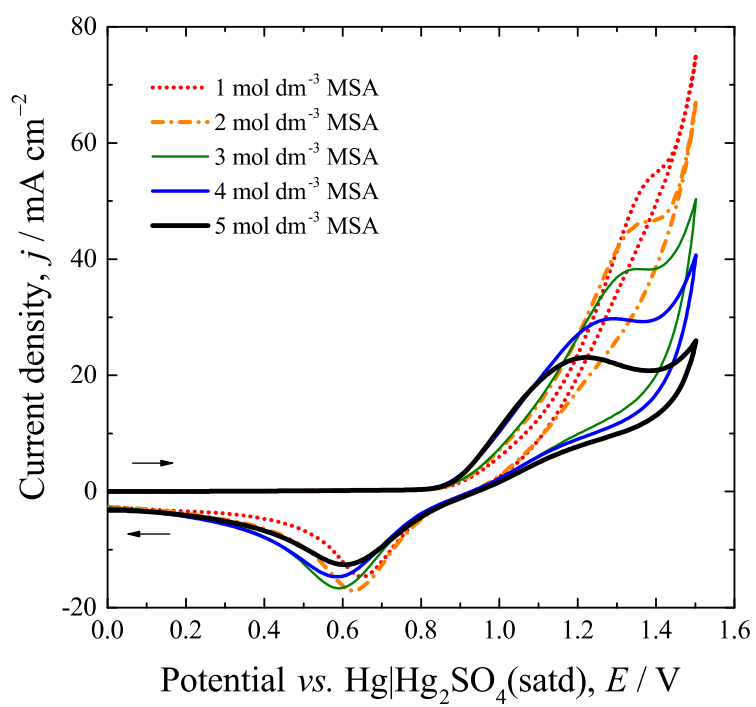


**Figure 5.**

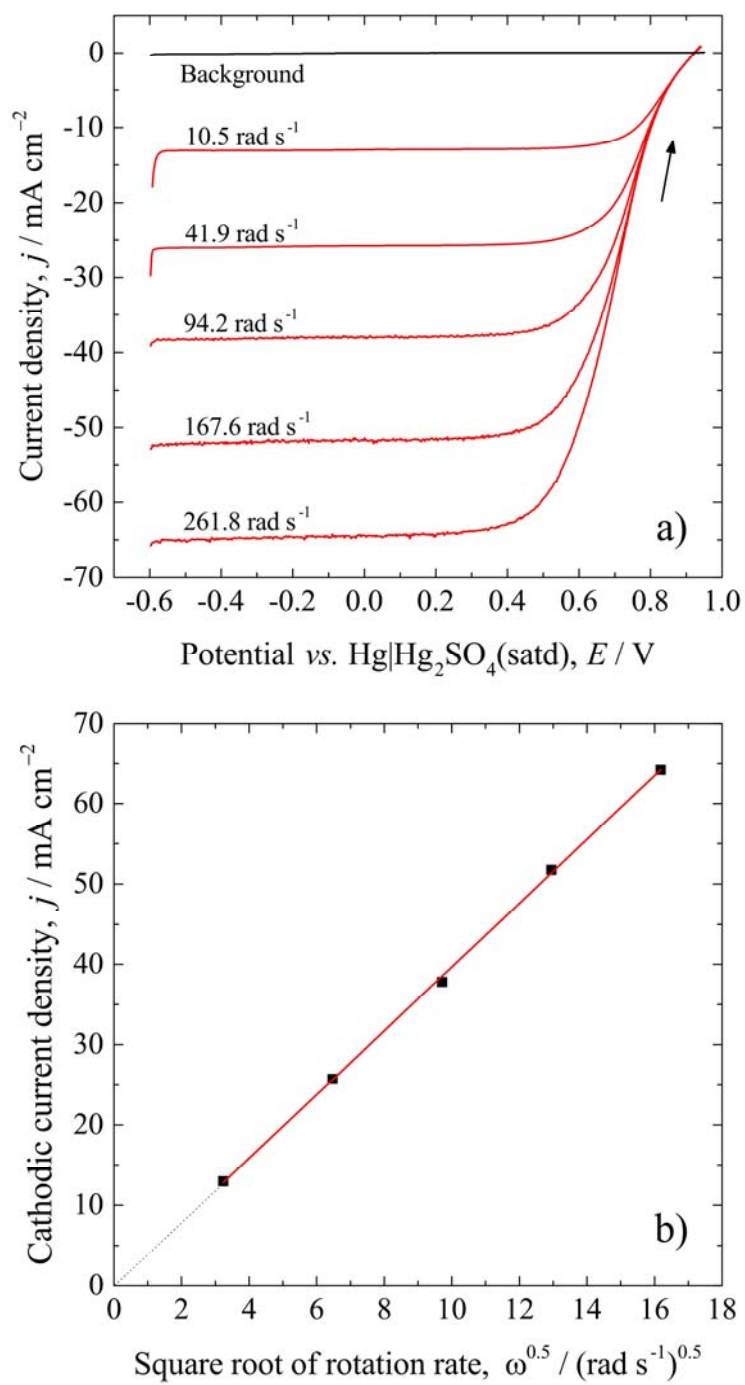




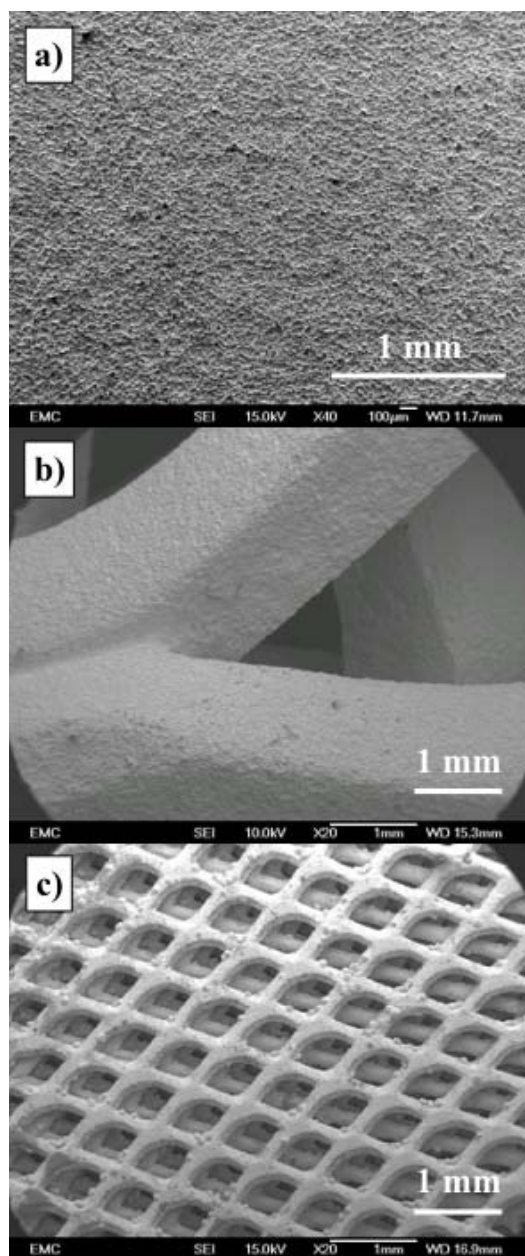
**Figure 6.**



**Figure 7.**



**Figure 8.**



**Figure 9.**

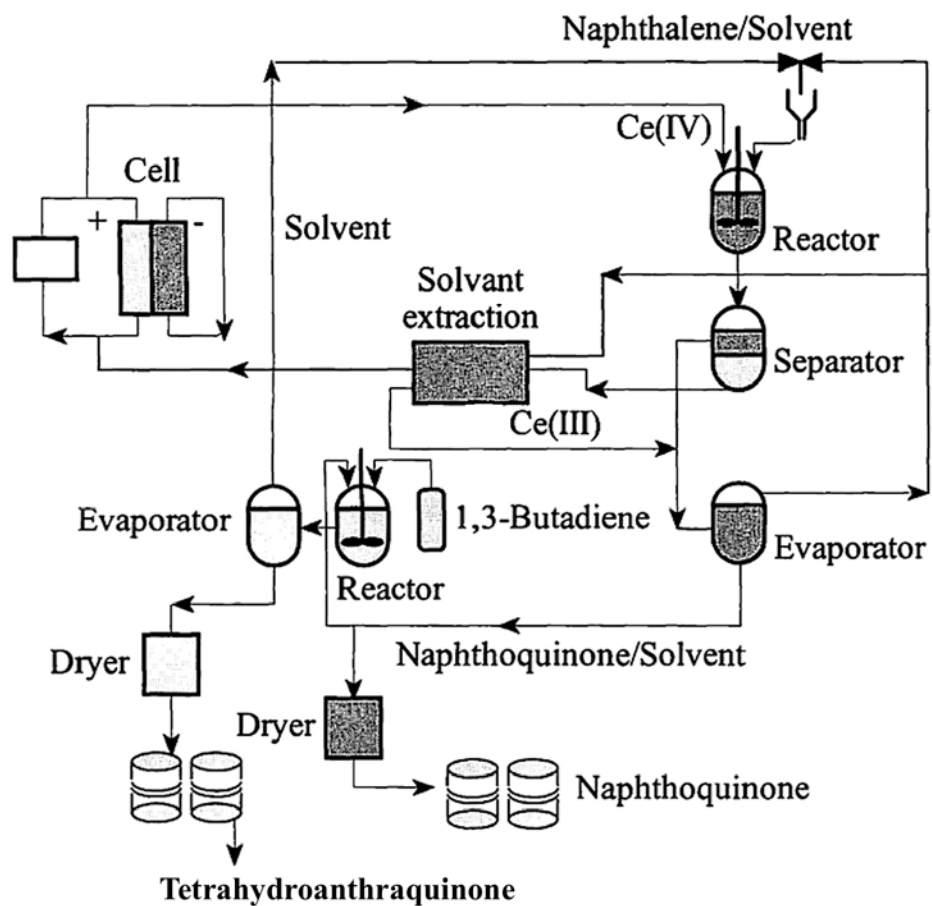
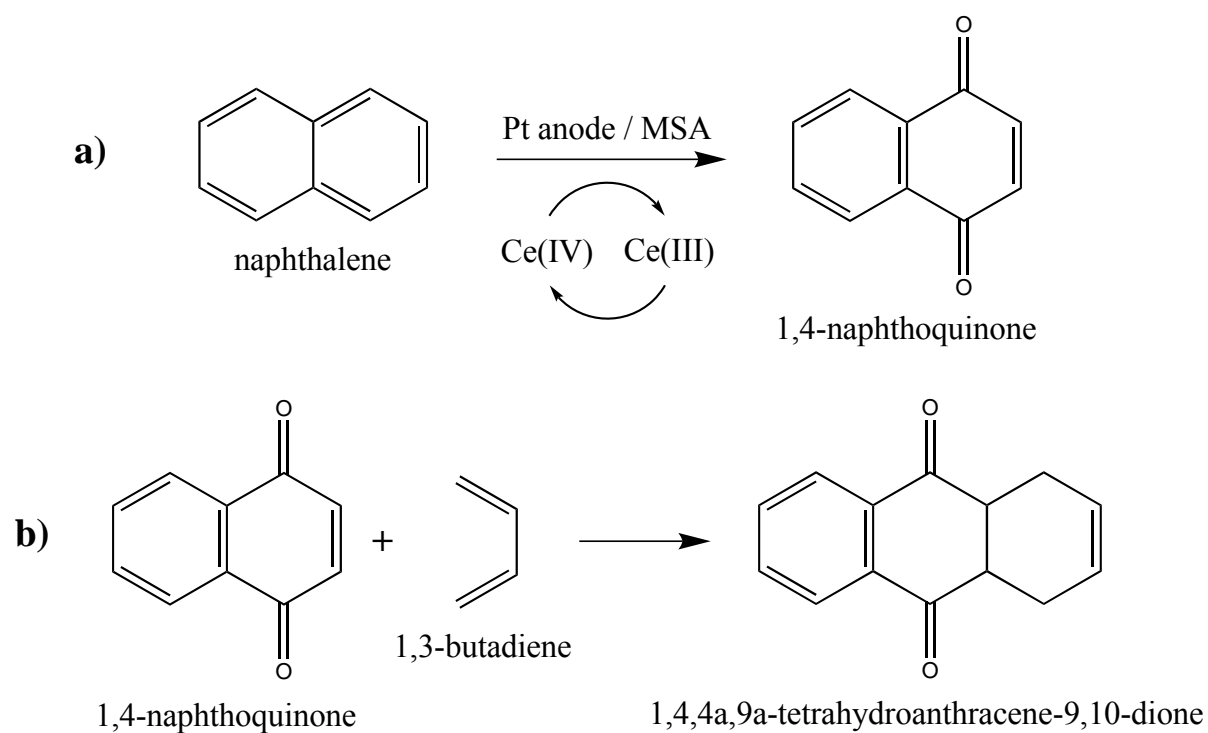
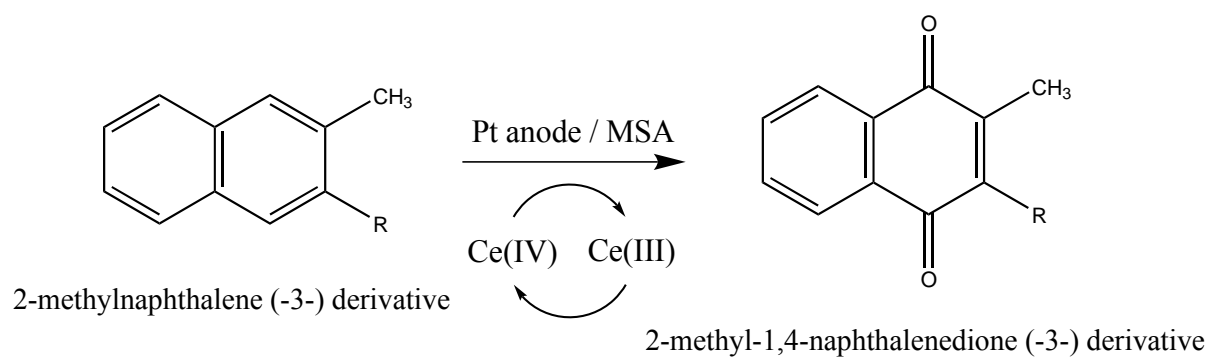


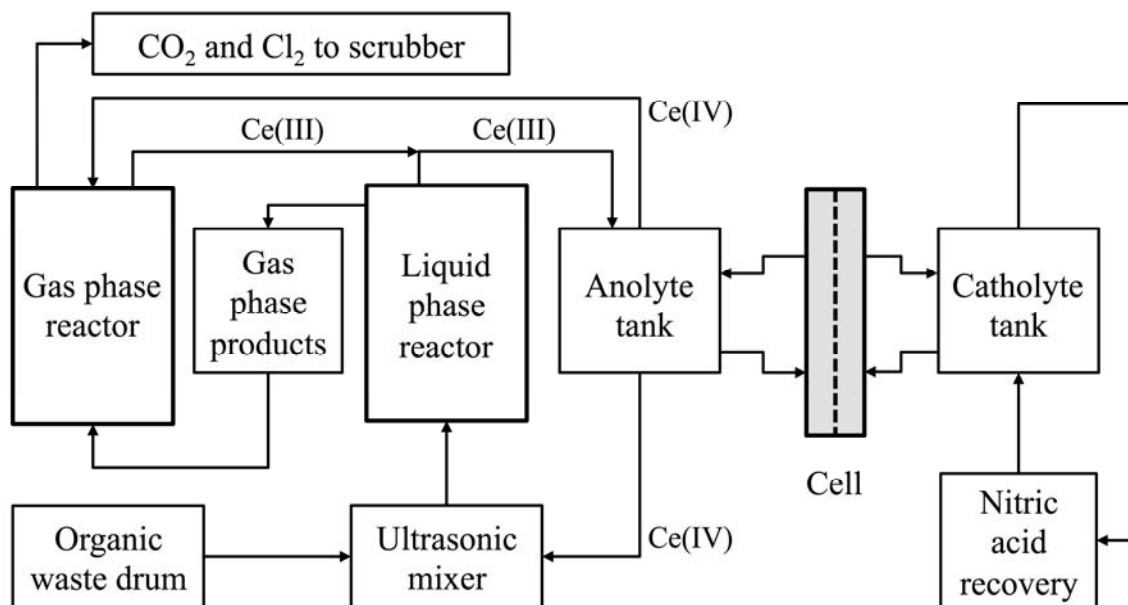
Figure 10.



**Figure 11.**

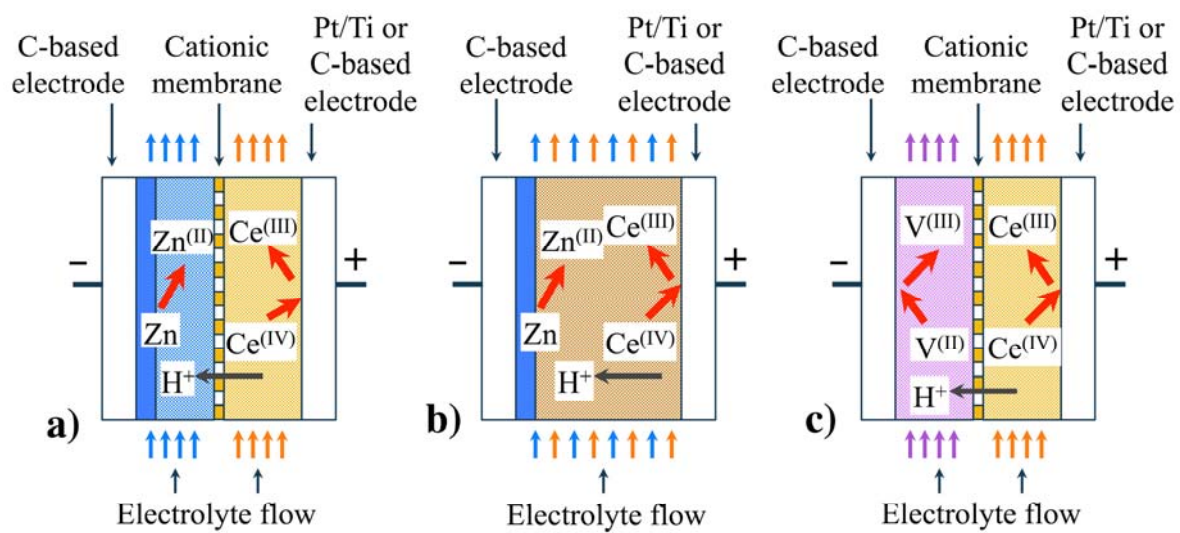


**Figure 12.**

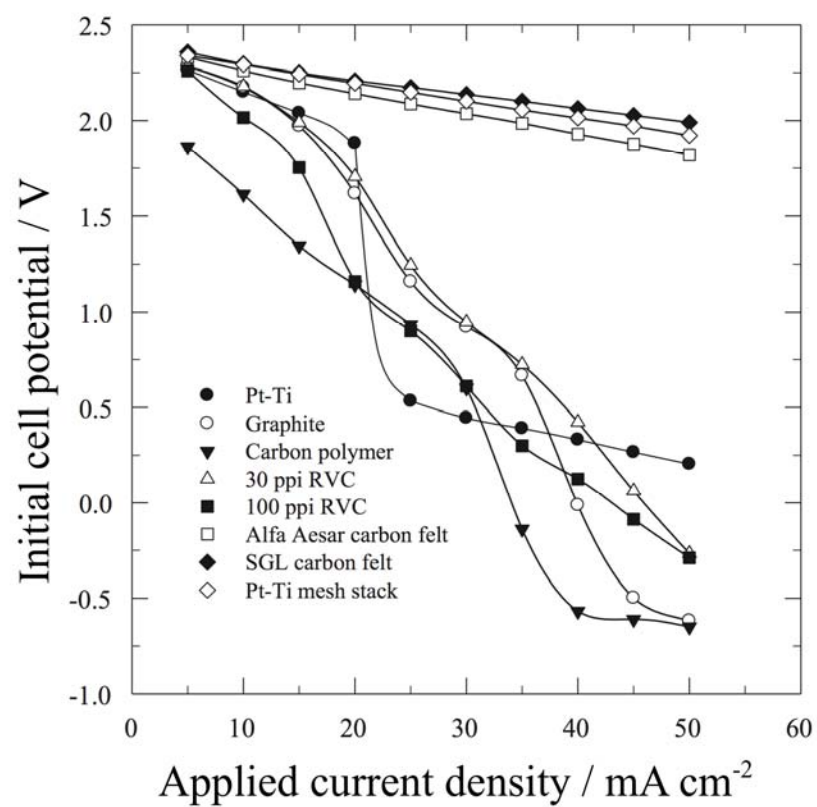


**Figure 13.**

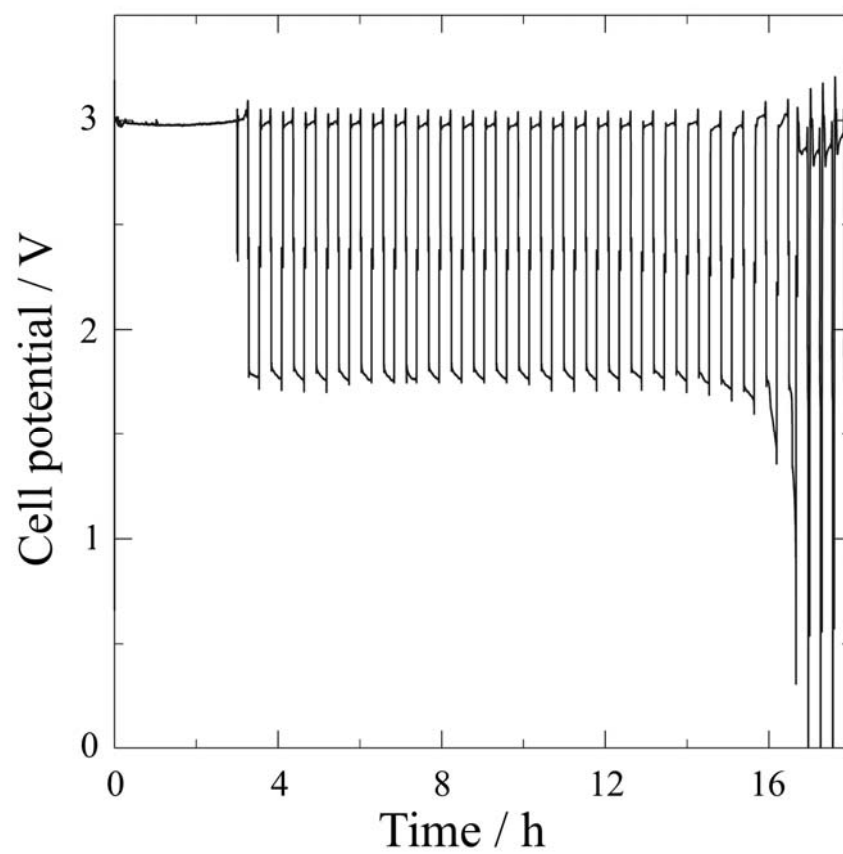




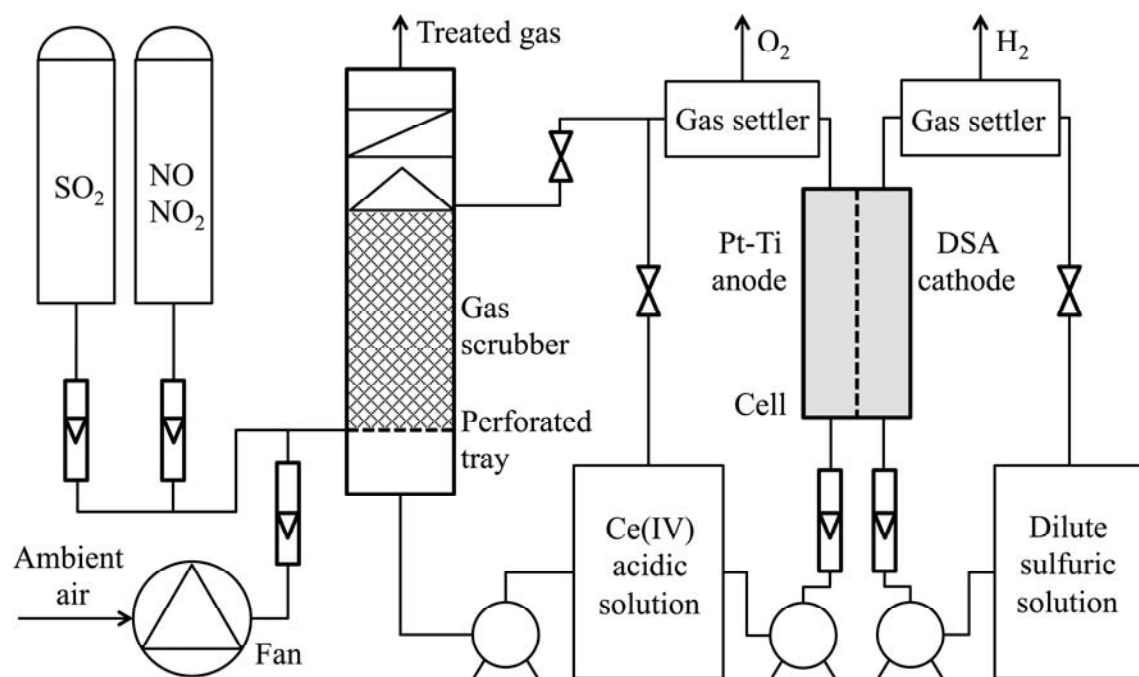
**Figure 14.**



**Figure 15.**



**Figure 16.**



**Figure 17.**