



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.

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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 received relatively little attention in the literature and no attempt has been made to bring together expertise from an electrochemical engineering perspective or to describe the factors that govern performance. A general scheme of known and potential applications of the Ce(III)/Ce(IV) with two major drivers is shown in Fig. 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],

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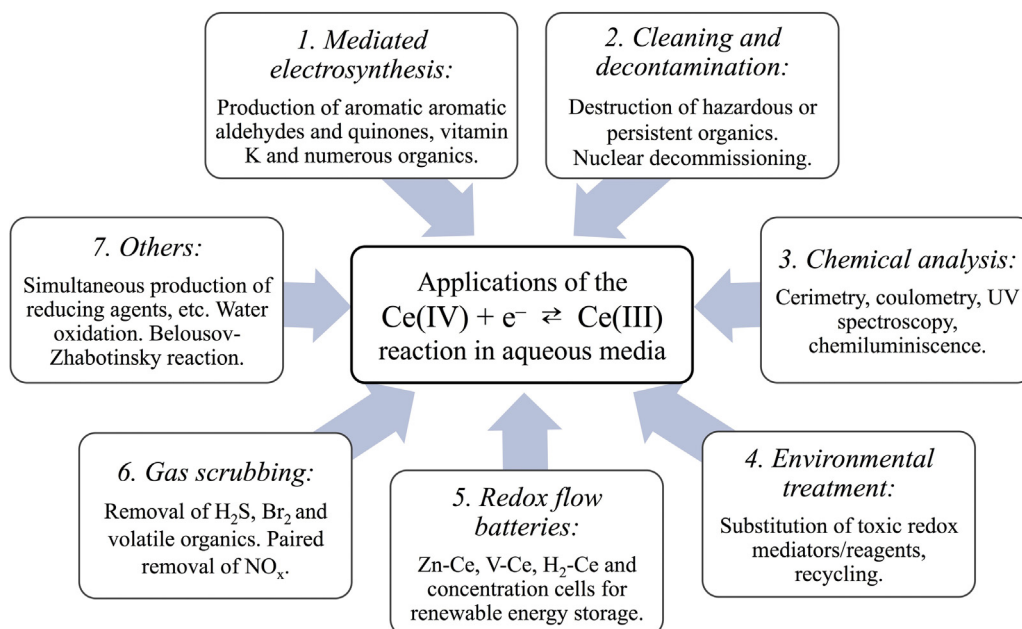


Fig. 1. The Ce(III)/Ce(IV) redox reaction and its applications, indicating section numbers in this review.

polyaromatic compounds to quinones [11], the oxidation of naphthalene derivatives to tetrahydroanthraquinone [11] and vitamin K₃ [12], as well as the destruction of organic contaminants [13]. Ce(IV) ions can be recovered and reused efficiently and have 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 Ce(IV) can completely destroy organic compounds to CO₂ and water, without harmful emissions.

The process 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, CH₃SO₃H) 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 to realise cost effective structures from diverse electrode materials and forms at a variety of scales.

China presently accounts for 97% of the production of rare earths, creating some market strain and concerns over 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(III)/Ce(IV) redox couple

2.1. The history of developments in soluble cerium species

As seen in Fig. 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 Fig. 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

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