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Electroanalytical chemistry of lanthanides and actinides

Abstract: The electrochemical properties of lanthanides (Ln) and actinides (An) are reviewed. This review summarizes papers from 1986 to 2011 with a primary focus on the electrochemical and redox properties of Ln/An elements in aqueous solution and their responses to a variety of electrode materials including Hg, Hg films, solid electrodes, modified carbon paste, and microelectrodes. A section is also devoted to the electrochemical properties and responses of Ln and An in nonaqueous and mixed solvent systems.

Keywords: electrochemistry; electrodes; f-elements; plutonium; pre-concentration.

[a]This work is dedicated to the memory of Prof. James O. Schenk, who passed away on January 31, 2013

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Introduction

Electroanalytical chemistry is a general term covering a wide variety of techniques that investigate the electrical properties of an electroactive analyte in solution. Electroanalytical techniques have many advantages over other detection systems, namely low cost, low detection limits, tunability to specific oxidation states for an analyte, and characterization of electrochemical information for the system under study (Skoog et al. 1997). Some of the information includes, but is not limited to, kinetics, rates and amounts of adsorption, stoichiometry, and rates of electron transfer (Skoog et al. 1997). Conducting a literature search on the electrochemistry of f-elements yields relatively few references. The reason for this scarcity of research is that although lanthanides (Ln) and actinides (An) are electroactive, their electrochemical properties are challenging to exploit, especially in aqueous solutions (Gao 1986).

Historically, the separation of trivalent f-elements has been a challenge due to similarities in their chemical behavior, making the determination of individual members of the f-element group difficult by electroanalytical techniques with only a few exceptions (Gao 1986, Nash and Jensen 2000). Despite these difficulties, progress has been made; new radioelectroanalytical approaches developed in the last 20 years have focused on exploiting the redox behavior of Ln and An to facilitate their separation. A review of current knowledge regarding the electrochemical properties is thus warranted. There are a number of acronyms used throughout this article, and a list of all acronyms used is included in Table 1 to aid the reader.

Summary of previous reviews of Ln and An electrochemistry

In 1966, the electrochemistry of Ln and An was reviewed by Ryabichicov and Ryabukhin, as translated by Aladjem (1970). In 1976, Herman and Rairden did an extensive review of Sc, Y, and Ln. Their review focused on the polarography in both aqueous and nonaqueous solutions along with polarographic characteristics and kinetic properties. O'Laughlin's (1979) short review on the polarography of Ln focused on separation and determination techniques and concluded that polarography was not an ideal technique for separation given the similar chemistries. In 1986, Gao reviewed the polarography of rare earths, focusing on detection *via* the addition of complexing ligands. More recently, Binnenmans (2007) review discussed the effects of solution conditions in ionic liquids (ILs) on Ln and An electrochemistry. Information on the reaction of f-elements with water was also provided, which suggested that pure metals cannot be deposited electrochemically in ILs.

Mudring and Tang's (2010) review covered the electrochemistry of Ln and An in ILs. Findings include deposit morphology, temperature dependence, deposition potential, and redox potentials for U along with other f-elements. In general, the review supports the use of ILs as electroanalytical solvents due to their wide electrochemical range, large ion conductivity, and ability to dissolve the f-elements. Because ILs were only recently reviewed,

Table 1 List of acronyms.

Acronym	Full description
Ln	Lanthanides
An	Actinides
IL	Ionic liquids
H/SMDE	Hanging/static mercury drop electrode
DME	Dropping mercury electrode
MFE	Mercury film electrode
CP	Carbon paste
MCP	Modified carbon paste
18-Crown-6	1,4,7,10,13,16-Hexaoxacyclooctadecane
CV	Cyclic voltammetry
ASV	Anodic stripping voltammetry
GC	Glassy carbon
PVC	Polyvinylchloride
LSV	Linear sweep voltammetry
ISE	Ion-selective electrode
LOD	Limit of detection
MWCNT	Multiwalled carbon nanotubes
HIBA	α-Hydroxyisobutyric acid
TBA	N-(1-Thia-2ylmethylene)-1,3-benzothiazole-2-amine
HDEBH	N'-(2-Hydroxy-1,2-diphenylethylidene) benzohydrazide
BMIM	1-Butyl-3-methylimidazolium
EMITFSI	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
BMPTFSI	1-n-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
PIPES	Piperazine-N,N'-bis(2-ethanesulfonic acid)

the focus of this review is to summarize the progress on electrochemistry of Ln and An since 1986, emphasizing aqueous and mixed solvent solutions.

Early voltammetric assessments of the f-elements

Since Professor Jaroslav Heyrovsky invented the polarographic method in 1922, Hg has been the electrode material of choice for investigations in the negative potential window (Galus and Meites 1975). Thus, nearly all early electroanalytical assessments of the f-elements were completed using pure mercury electrodes, typically a hanging mercury drop electrode (HMDE) or dropping mercury electrode (DME). These mercury electrodes were desirable for radiopolarographic analysis, a technique in which drops were collected and the concentration of analyte was determined *via* nuclear counting (Samhoun and David 1979, David et al. 1981). Mercury can be advantageous for these techniques, as these electrodes are

known to provide a rapidly renewable and smooth surface and a high overpotential for hydrogen, thus extending the potential range in aqueous solutions, and it has the ability to form amalgams, or more specifically, alloys with one or more metals (Kowalski et al. 1987, Mikkelsen and Schroeder 2003). The overpotential value for hydrogen has been reported at -0.85 V in aqueous solution (Bard and Faulkner 2001). However, this value is dependent on solution conditions because each elementary step in an electrochemical mechanism is subject to contributions from resistance, concentration, ionization, and polarization overpotentials creating variability in measurements (Ammar and Hassanein 1960). The mercury overpotential was advantageous during aqueous f-element studies based on the inherent reduction potentials of these elements; however, most early works on Ln and An were not done in purely aqueous media. Early voltammetric analysis of these metals was done in the presence of a complexing ligand, such as 1,4,7,10,13,16-hexaoxacyclooctadecane (18-Crown-6) or acetate (Maly 1967, David and Bouissieres 1968, Sipos and Galus 1971, Herman and Rairden 1976, Yamana et al. 1983). The addition of complexing ligands allows for observations of the redox properties of f-element metals because the metals interact with the ligand at the electrode surface, typically at a less negative potential than would be observed for the f-element cation. Several works observed the existence of a divalent state and the ability of these metals to form amalgams in their presence (David and Bouissieres 1968, Herman and Rairden 1976). A review of the f-elements by Herman and Rairden (1976) indicated that the reduction of the Ln and An is not a simple process, with several references to works noting hydrogen gas formation and/or hydride and oxide formations, all with contributions to the voltammetric signals observed.

Later electroanalytical assessments shifted to new modified electrodes with better sensitivity, stability, and lower environmental toxicity. These electrodes included the mercury film electrode (MFE) and the modified carbon paste (MCP). Commonly, the MFE based on glassy carbon (GC) is chosen for electroanalytical studies due to the substance's chemical inertness, useful potential range, low residual current, readily renewable surface, and low cost (Economou and Fielden 2003); however, other base materials have been and can be used for a wide variety of applications. Besides the utility of the electrode, the mercury content of solutions tested with this electrode held considerable lower mercury contamination, which became an important characteristic as electroanalysis of environmental samples became more prominent. As the desire to reduce mercury from

electroanalysis arose, the MCP became more widely used. The many current utilities and modifications of carbon paste (CP) have been reviewed in the current millennium by Švancara et al. (2009). Similar to their pure mercury predecessors, both MFE and MCP have proven to be very effective in the determination of redox characteristics of the f-elements in a range of solution conditions. A summary of some of these applications and findings is presented later.

As this review is broken down by electrode types, it is useful to include a table of working potential ranges for the different electrodes. Table 2 is a summary of the potential ranges. Upon observation, two points are worth noting. First, Hg has a larger negative potential window than the other elements, thus its wide usage with Ln and An. Second, the potential range expands when the electrode material is used in nonaqueous solvents.
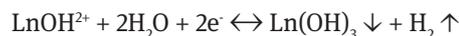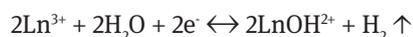
Table 2 Summary of electrode potential ranges.

Material	Type	Conditions	E range (V)	Metals	References
Mercury					
	HMDE	Acetone/18-Crown-6	0.4 to -2.3	Eu	Gao and Guan 1988
	HMDE	$NaClO_4$	-1.2 to -1.5	Yb	Xiaoquan et al. 2000
	HMDE	$KMnO_4$	-1.2 to -1.5	Yb	Xiaoquan et al. 2000
	DME	CCl_4/TMACl	-2 to -2.4	Ac	Yamana et al. 1983
	DME	$KMnO_4$	-1.15 to -1.55	Yb	Xiaoquan et al. 2000
	DME	Mordant red/ammonium buffer	-0.5 to -1	Tb	Lee et al. 1997
	DME	Acetate buffer/mordant blue	-0.2 to -1	U	Wang and Zadeii 1987
	DME	PIPES/SVRS	-0.8 to -1.2	Yb	Wang and Zadeii 1986
	DME	Aqueous	-2 to 1.84	Cf/Gd/Sm	Musikas et al. 1981
	Hg pool	Acetate buffer	5	Cf/Es/Fm	Maly 1967
	Hg pool	Aqueous	-1.6 to -2.8	Ln	Yamana and Moriyama 1997
	MFE	Nafion/NH_4Cl	0 to -1.5	Eu	Ugo et al. 1991
	MFE	Nafion/NH_4Cl or in NH_4NO_3	0 to -1.5	Yb	Ugo et al. 1991
	MFE	KNO_3/chloranilic acid	-0.05 to 0.25	U	Piech et al. 2007
	MFE	LiCl	-2.5 to 1.5	Ln	Schumacher et al. 2010
Carbon					
	MCP-HIBA	LiCl	0.8 to -0.4	Ln	Schumacher et al. 2011a–c
	Sal-SAMMS	Acetate buffer or NH_4Cl	0 to -0.95	Eu	Yantasee et al. 2006
	CP	Acetate buffer	-0.3 to -0.8	Ho	Li et al. 2004
	CP	Acetate buffer	-0.3 to -0.8	Ce	Li et al. 2006
	CP	NaAc-Hac/KHP buffer	-0.3 to -0.9	Ce	Liu et al. 2005
	MCP-MWCNT	KCl	-0.02 to 0.18	Tb	Ganjali et al. 2010
	MCP-MWCNT	KCl	0.05 to 0.25	Er	Norouzi et al. 2010
	MCP-MWCNT	KCl	-0.02 to 0.28	Ho	Ganjali et al. 2009
	MCP-MWCNT	KCl	0 to 0.16	Ho	Faridbod et al. 2010
	Graphite	Cs_2NpCl_6/HMPA	0 to -2	Np	Martinot et al. 1995
	Graphite	Cs_2NpCl_6/DMF	0 to -3.5	Np	Martinot et al. 1995
	GC	BMPTFSI or EMITFSI	1 to -1.5	Eu	Yamagata et al. 2006
	GC	BMPTFSI	0 to -2	Yb	Yamagata et al. 2006
	GC	BMPTFSI	0 to -3	Sm	Yamagata et al. 2006
	GC	Molten NaCl-2CsCl	-0.5 to -2.1	U	Nagai et al. 2005
	Carbon fiber	HIBA/LiCl	-0.5 to 1.5	Ce	Toyoshima et al. *2008*
	Carbon fiber	LiCl	-2.5 to 1.1	Ln	Schumacher et al. 2011a–c
Platinum					
	Pt	$ThCl_4$/molten DMSO	-0.15 to 0.65	Th	Martinot et al. 1995
	Pt	Cs_2NpCl_6/molten DMSO	0 to -2.3	Np	Martinot et al. 1995
	Pt	Molten $DMSO_2$/$Cs_2UO_2Cl_4$	0 to -1.5	UO_2	Martinot et al. 1990
	Pt	Molten $DMSO_2$/Cs_2UCl_6	0 to -1.3	U	Martinot et al. 1990
Gold					
	Au fiber	H_3PO_4	-0.4 to 1.4	Ln	Pourjavid et al. 2009a,b
	Au fiber	H_3PO_4	-1 to 2	Ln	Pourjavid et al. 2010
	Au fiber		0 to 0.14	Ln	Ganjali et al. 2007

Amalgamation studies of f-elements

Between the 1950s and the 1990s, most electroanalytical investigations of f-elements involved polarographic or radiopolarographic analysis of amalgams with an Hg pool serving as the working electrode or cathode. These studies were carried out in a controlled pH range of 2.0–4.0 (David and Bouissieres 1968, Musikas et al. 1981, Yamana et al. 1983, David et al. 1990a,b, Yamana and Moriyama 1997, 1998), except for David et al. 1990a,b, who conducted studies in the 6.0–7.0 range. Background electrolytes were typically 0.1–1.0 M alkali metal chlorides or perchlorates (David and Bouissieres 1968, Musikas et al. 1981, Yamana et al. 1983, David et al. 1990a,b, Yamana and Moriyama 1997). Several studies also used the complexing ligands of citrate and acetate (David and Bouissieres 1968, David et al. 1990a,b) or 18-Crown-6 (Yamana et al. 1983, Yamana and Moriyama 1997, 1998).

A few observations become apparent as a result of analyzing amalgamation studies. Several investigators discovered and confirmed the stable divalent oxidation states for various An because amalgamation techniques give the reduction potentials from the most stable oxidation state (David and Bouissieres 1968, Musikas et al. 1981, David et al. 1990a,b, Yamana and Moriyama 1997). In general, An were found to reduce *via* a two-step mechanism compared with a single-step process for Ln. A direct correlation was observed between the reduction potential of the metal and the stability constant of any metal-ligand complex in solution. Amalgamation was also observed to follow a first-order kinetic rate expression. As amalgamation techniques report reduction potentials from the most stable oxidation state in solution to amalgamated metallic states in mercury, one would expect to observe large negative potentials to overcome the stability of the metallic oxidation state of the f-element. Table 3 confirms that large negative potentials are required for Ln/An reduction. Table 3, which is a compilation of electrochemical information from Bard et al. (1985), David et al. (1990a,b), and Yamana and Moriyama (1997) shows that the reduction of the metals are well within the potential window for hydronium reduction, which leads to a large background current and makes operating in aqueous solutions challenging. Although general metal reduction schemes are proposed, it is noteworthy that these are based on the comparison of cyclic voltammetry (CV) and have not been subjected to a rigorous kinetic investigation for validation. As amalgamation experiments are time-consuming, i.e., hundreds of minutes, the technique is not ideally suited for kinetic measurements. However, other electroanalytical techniques that operate on shorter timescales could provide

mechanistic information. Additionally, the CVs show that in the case of Ln, a potential mechanism for reduction based upon a previously reviewed work (Herman and Rairden 1976) is as follows (Musikas et al. 1981):

$$2Ln^{3+} + 2H_2O + 2e^- \leftrightarrow 2LnOH^{2+} + H_2 \uparrow$$

$$LnOH^{2+} + 2H_2O + 2e^- \leftrightarrow Ln(OH)_3 \downarrow + H_2 \uparrow$$

Although this potential mechanism accounts for many of the observations that occur in the reduction of Ln and An, to date, there is no consensus on the actual elementary steps of the mechanism. It may be stated, based on the previously mentioned reviews, that Ln reduce *via* a one-step 3 e$^-$ transfer (Herman and Rairden 1976). Another possibility is that charge transfer could potentially occur through a ligand bridge. The fact that halide anions can cause anion-induced adsorption on Hg is well known (Bard and Faulkner 2001). As seen in Tables 2 and 3, halide anions are used as supporting electrolyte, although other supporting anions such as perchlorate are also used. It would be worthwhile to explore the effects of supporting electrolyte on the reduction mechanism of Ln and An. Regardless, knowing the actual mechanism would greatly enhance our ability to develop an electrochemical separation technique, as technological advances allows us to work at ultratrace levels.

Electrochemistry of f-elements on Hg and Hg film electrodes

The next studies utilize a DME (Ugo et al. 1991, Tamrakar and Pitre 2000), hanging/static mercury drop electrode (H/SMDE) (Wang and Zadeii 1986, 1987, Lee et al. 1997, Xiaoquan et al. 2000, Piech et al. 2007), or MFE (Ugo et al. 1991, Piech et al. 2007, Schumacher et al. 2010, 2011b,c) to detect f-elements (Wang and Zadeii 1986, 1987, Ugo et al. 1991, Lee et al. 1997, Tamrakar and Pitre 2000, Xiaoquan et al. 2000, Piech et al. 2007) or pre-concentrate (Schumacher et al. 2010, 2011a–c) f-elements. Solution and sample compositions varied from environmental analysis to neat solutions. The pH range and background electrolyte concentration/composition, shown in Table 4, are in general agreement with amalgamation studies. The most prevalent technique used for detection of Ln and An was anodic stripping voltammetry (ASV), with sweep and potentiostatic techniques used in the pre-concentration studies (Schumacher et al. 2010, 2011a–c).

The general observations for DME, H/SMDE, and MFEs are that Ln and An exhibit linear accumulation at

Table 3 Summary of electrochemical data of Ln and An with Hg electrodes.

Element	Metallic radius (Å)[a]	Medium[b]	pH[b]	E^0, V vs. SHE[c]	$E_{1/2}$ vs. SHE[b]	$E_{1/2}$ vs. NHE[a]	Mechanism[b]
La	1.88			-2.38		-1.75	
Ce	1.83	0.1 M LiClO$_4$	2.2/3.2	-2.34	-1.84±0.01	-1.83	3→0 irr
Pr	1.83			-2.35		-1.88[d]	
Nd	1.82			-2.32		-1.83[d]	
Pm	1.81			-2.29		-1.79[d]	
Sm	1.80	0.1 M LiClO$_4$	2.95/3.65	-2.30	-1.72±0.01	-1.71	2→0 irr
Eu	2.04	0.1 M LiClO$_4$	3.0/5.8	-1.99	-1.71±0.01	-1.70	2→0 r
Gd	1.80	0.1 M LiClO$_4$	4.0/5.5	-2.28	-1.78±0.01	-1.78	3→0 irr
Tb	1.78	0.1 M LiClO$_4$	3.3/3.4	-2.31	-1.74±0.01	-1.73	3→0 irr
Dy	1.77			-2.29		-1.79[d]	
Ho	1.77	0.1 M LiClO$_4$		-2.33	-1.78±0.01	-1.77	3→0 irr
Er	1.76			-2.32		-1.74[d]	
Tm	1.75			-2.32		-1.73[d]	
Yb	1.94	0.1 M LiClO$_4$	2.0/3.5	-2.22	-1.81±0.01	-1.81	2→0 irr
Lu	1.74	0.1 M LiClO$_4$	3.5	-2.30	~-1.69	-1.68	3→0 irr
Ac	1.88		2.5/3.2	-2.21[e]	-1.96±0.02	-1.91	3→0 irr
Th				-1.83			
Pa		1 M HCl[e]		-1.47			
U	1.54	0.005 M (CH$_3$)Cl$_4$	1.5/3	-1.65	-1.65±0.05	-1.65	3→0 irr
Np	1.50			-1.77[e]		-1.78[d]	
Pu	1.52			-2.00		-1.99[d]	
Am	1.73	0.1 M LiCl	1.8/2.25	-2.07	-1.60±0.01	-1.72	3→0 irr
Cm	1.74	0.1 M LiCl	1.8/2.26	-2.06	-1.61±0.01	-1.77	3→0 irr
Bk	1.70	0.1 M LiCl	1.8/2.27	-2.00	-1.63±0.01	-1.63	3→0 irr
Cf	1.69	0.1 M LiCl	1.8/2.28	-1.91	-1.51±0.01	-1.51	3→0 r
Es	1.98	0.1 M LiCl	1.8/2.29	-1.98	-1.46±0.01	-1.46	3→0 r
Fm	1.97	0.1 M LiCl	2.4	-2.07	-1.49±0.01	-1.47	3→0 irr[e]
Md		0.1 M LiCl	2.4	-1.74	-1.51±0.01		3→0 irr[e]
No				-1.26[e]			
Lr				-2.06[e]			

[a]Yamana and Moriyama 1997.
[b]David et al. 1990a,b.
[c]Bard et al. 1985.
[d]Estimated from Yamana and Moriyama 1997.
[e]Updated from Edelstein et al. 2010.
irr, irreversible; r, reversible.

the surface of the electrode until saturation is achieved. In the case of Ln, the sequence of film formation *in situ* (i.e., the formation of the mercury film with the analyte present and adsorbing during film formation) vs. *ex situ* (i.e., the formation of the mercury film with no analyte present in solution and the analyte added to solution after film formation) lowered the detection limits by well over an order of magnitude in the case of *ex situ* (Schumacher et al. 2010, 2011a–c). Although this phenomenon was observed, the reason for this behavior is still under investigation. Changing the background electrolyte anion improved the detection limits for An (Tamrakar and Pitre 2000). Exploiting the electrochemistry of the complexing ligand improved the detection of Ln and An down to the ultratrace level at much higher pH range (6.0–9.0) (Wang and Zadeii 1986, 1987, Lee et al. 1997). Not unexpectedly, the use of ASV lowers the detection limit for both Ln and An by up to four orders of magnitude, and it is possible to detect down to the subnanomolar range (Wang and Zadeii 1986, 1987). Depending on solution conditions, sweep waveforms can be preferential to differential pulse. The use of DME, H/SMDE, or MFEs allows the timescale of analysis to dramatically decrease compared with amalgamation studies. Most experiments required only minutes to detect or pre-concentrate compared with hours for the amalgamation studies. One of the benefits of this decrease in experimental time is that it now allows for the kinetic study of the reduction mechanism. Although each of these

Table 4 Summary of electrochemical data of Ln and An on mercury films.

Metal	Electrode	E (V)	Background electrolyte	Detection limit (M)	Waveform	References
Yb	DME/SMDE	-1.48	0.1 M NaClO$_4$	10^{-7}	LSP	Xiaoquan et al. 2000
Eu/Yb	MFE (Nafion)	-0.67/-1.5	0.1 M NH$_4$NO$_3$	10^{-8}	DPV	Ugo et al. 1991
La, Eu, Tb, Yb	HMDE	-0.7 to -0.8	1.0 M NH$_3$ buffer	10^{-10}	ASV	Lee et al. 1997
Y, Dy, Ho, Yb	HMDE	-1.00	0.02 M PIPES	10^{-10}	ASV	Wang and Zadeii 1986
La, Nd, Eu, Gd, Ho, Lu	MFE	-2.20	0.1 M LiCl	10^{-11}	LSV	Schumacher et al. 2010
U	DME	-0.24	0.1 M KSCN	10^{-12}	DPASV	Tamrakar and Pitre 2000
U	Hg(Ag) film	-0.8	0.1 M KNO$_3$	10^{-10}	DPSV	Piech et al. 2007
U	HMDE	-0.56	0.05 M Ac buffer	10^{-10}	ASV	Wang and Zadeii 1987

electrochemical techniques is sensitive, it is not possible to determine any isotopic information *via* the use of electroanalytical techniques. If isotopic information is desired, as would be the case in nuclear forensic analysis, a follow-on detection method such as radiometric counting or mass spectrometry would be required to elucidate the isotopic abundances (Schumacher et al. 2010).

The role of pH is of concern when working with Ln and An. Above pH 5.0, metal hydrolysis and precipitation becomes the dominant reaction in solution when working with Ln and An in an aqueous solution (Nash and Jensen 2000). This limits the pH range in which electroanalytical measurements can be made. At low pH values, background current from water hydrolysis increases at the negative potentials required to reduce Ln and some An. This increase in background current can make analyte signal determination problematic and challenging. Additionally, H$_2$ gas evolution also increases, which can cause disruptions in the formation of an Hg film. Some thought must therefore be given to determine the optimal pH to conduct experiments.

A final note on observable trends when working with Hg: the presence of O$_2$ in solution will oxidize the surface of Hg, thus reducing the effective surface area available. All working solutions are typically purged with an inert gas, such as Ar, before conducting any experiments. During experiments, the inert gas is blown over the solution in the electrochemical cell to minimize O$_2$ interference during the conduct of the experiment.

Solid electrodes

Given the inherent toxicity of Hg, there is growing interest in pre-concentrating and/or detecting and separating Ln and An with other electrode materials. Solid electrodes for detection of Ln and An include Pt-, Ti-, and C-based electrodes. Voltammetric responses vary with the electrode material used, thus opening a larger untapped field of study.

It should be noted that within this field of solid electrodes, an entire series of studies that deal with Ln and An in organometallic complexes has been published. These ligands have multiple redox centers; thus, it is difficult to elucidate the electrochemical characteristics of the Ln and An from those of the ligands. Therefore, this review acknowledges this body of work, but it is excluded from further discussion here because they constitute an independent field of study.

The studies reviewed cover the solid electrodes graphite (Kayasth 1993), Ti (Kim et al. 1994), GC (Clark et al. 2006, Yuan et al. 2006, Liezers et al. 2009), and a polyvinylchloride (PVC)-based ion-selective electrode (ISE) (Tyagi et al. 2010). Solution compositions varied from seawater to blood serum and were generally in the acidic pH range (<6.0). One of the major findings is that in 4% NaCl solutions, Ln exhibit a tendency to electrodeposit on graphite electrodes at potentials much lower than predicted by the Nernst equation (Kayasth 1993). Clark et al. (2006) followed by Liezers et al. (2009) were able to pre-concentrate, separate, and detect attomolar levels of Pu and U on an anodized GC electrode using inductively coupled plasma mass spectrometry by exploiting the unique electrochemical properties of U and Pu. By modifying a GC electrode with carbon nanotubes and a Nafion coating, Yuan et al. (2006) detected Eu^{3+} in an environmental sample *via* the Eu^{3+}/Eu^{2+} redox couple. The technique showed enhanced selectivity for Eu^{3+}, although other rare earths also were adsorbed. Tyagi et al. (2010) developed a Eu^{3+} ISE utilizing *p-tert*-butylcalix[4]arene derivative (L) on a PVC-based electrode. This ISE was applicable over a large pH range and would operate both in aqueous and nonaqueous solutions.

These studies highlight that although the electrochemical properties of Ln and An in aqueous solution can be challenging to exploit, creative solutions abound. An interesting observation deserving further systematic

investigation is the underpotential deposition, a term coined by Herzfeld in 1914 on graphite which was observed by Kayasth in 1993. Kayasth observed that more than 60% of Ln present was able to adsorb to a 2-mm graphite rod in a stirred solution of 4% NaCl at pH 1.5. The removal from the electrode was accomplished by stirring in 2 M HNO_3. Although no kinetic parameters were measured, the rate of adsorption is slow, given the electrolysis time (~15 h); however, if the mechanism of adsorption could be elucidated, then the possibility of potentially finding a catalyst to speed the reaction is available. The works of Clark et al. (2006) and Liezers et al. (2009) are good examples of how incorporating the electrochemical properties of An in an analytical process can greatly improve the chemical separations for follow on detection eliminating the need for multiple chemical separation steps. Yuan et al. (2006) is an excellent example of how modifications to an electrode can increase the sensitivity and selectivity for a particular analyte. By modifying the GC electrode with a carbon nanotube-Nafion film, the sensitivity to Eu^{3+} increased (Yuan et al. 2006). The properties of nanotubes will be discussed in the next section. In the case of Tyagi et al. (2010), incorporating a permselective membrane with an ionophore that is sensitive to Eu^{3+} opens a whole new avenue in the realm of sensor development for Ln and An, and will be discussed further in the following section.

Carbon and modified CP

CP electrodes are now widely used in electrochemical research. Many factors contribute to their popularity: low ohmic resistance, large potential window, and ease of modification, to name a few (Arrigan et al. 1994, Švancara et al. 2009, Vytras et al. 2009). Given the large negative reduction potentials required for Ln and An, one creative approach to pre-concentrate and/or detect f-elements is to exploit the redox properties of a metal-ligand complex through CP modification, which occurs in a more positive potential region as was highlighted earlier (Wang and Zadeii 1986, 1987, Lee et al. 1997); MCP electrodes are ideally suited for this type of approach (Li et al. 2004, 2006, Liu et al. 2005, Yantasee et al. 2006, Ganjali et al. 2009, 2010, Faridbod et al. 2010, Norouzi et al. 2010, Schumacher et al. 2011a–c). Table 5 summarizes the types of modifications and their results. CP electrodes can be modified in several ways including chemical pretreatment, *in situ* modification, dissolution in the binding liquid, or direct mechanical mixing of dry modifiers into the paste (Stozhko et al. 2008).

One major advantage of using an MCP electrode with f-elements is that it provides a more selective surface for separations. Work has been done using the preferential binding of Ln to the modifiers in MCPs; for example, Liu et al. (2005) created an MCP with two modifiers that increased the selectivity for Ce^{3+} when optimized to a limit of detection (LOD) for Ce^{3+} of 10^{-9} M. In addition to increasing the selectivity for individual Ln, work has also been focused on production of ISEs for Ln using multi-walled carbon nanotubes (MWCNT), nanosilica, and room temperature ILs along with ionophores as modifiers (Ganjali et al. 2009, 2010, Faridbod et al. 2010, Norouzi et al. 2010). The use of MWCNTs is growing because there are many advantages to the use of these structures as modifiers, such as their unique electronic structures,

Table 5 Summary of electrochemical data of Ln from CP and MCP electrodes.

Metal(s)	Electrode	Detection level (M)	Background electrolyte	Time (s)	References
La	MCP (HIBA)	10^{-15}	LiCl	300[a]	Schumacher et al. 2011a–c
Ce[b]	CP	10^{-6}	HAc-NaAc/KHP	120[a]	Li et al. 2006
Ce[b]	MCP (cetyltrimethylammonium)	10^{-10}	HAc-NaAc/KHP	120[a]	Liu et al. 2005
Eu	Screen printed carbon sensors	10^{-9}	NH_4Cl	180–600[a]	Yantasee et al. 2006
Tb	MCP ([BMIM]BF_4, MWCNTs, L)[c]	10^{-8}	Tb salts	16	Ganjali et al. 2010
Ho	MCP (ionophore, MWCNTs, nanosilica)	10^{-8}	Ho salts	10	Ganjali et al. 2009
Ho	MCP (TBA, MWCNTs)[b]	10^{-6}	Ho nitrate/ acetonitrile	13	Faridbod et al. 2010
Er	MCP (HDEBH, MWCNTs, [BMIM]BF_4, nanosilica)[c]	10^{-8}	Er salts	16	Norouzi et al. 2010
Sm, Eu, Tb, Ho, Yb, Y[b]	CP	10^{-10}	HAc-NaAc	120[a]	Li et al. 2004

[a]Cation pre-concentration; others represent detection time for sensor.
[b]Solution mixture of the cation(s) with alizarin complexone.
[c] L, *N'*-(2-Napthoyl)-8-(dimethylamino)naphthalene-2-sulfonohydrazide.

electrical conductivity, high specific surface area, and strong adsorptive abilities (Yuan et al. 2006). Overall, these MCP electrodes display remarkable selectivity and serve as durable sensors for Ln.

Another advantage to MCP electrodes is their potential in pre-concentration and detection of Ln and An. Luckily, this topic is one ripe for exploration. Work has been done with a variety of ligands, pasting liquids, and electroanalytical techniques showing little variation in results due to carbon's ability to be an inert conductor. Specifically, Schumacher et al. (2011) has done work using α-hydroxyisobutyric acid (HIBA) as a modifier that could pre-concentrate as little as 3.6×10^{-11} mol/m^3 of an f-element mixture (Schumacher et al. 2011a–c). Although previous work has shown carbonaceous material to be just as effective in pre-concentration, the use of an MCP significantly reduces the time needed for reaction from hours of contact to minutes (Faridbod et al. 2010, Schumacher et al. 2011a–c). As a final note, although all of these experiments were done under aqueous conditions, MCP electrodes can be used in nonaqueous/mixed solvent environments as well, further expanding their usefulness in Ln and An electrochemical analysis.

Microelectrodes

Microelectrodes, conventionally defined as electrodes with active dimensions in the tens of micrometers or less, have gained wide acceptance within the field of electrochemistry, due to their distinct advantages over conventionally sized (~3 mm) electrodes, namely, low ohmic drop, fast response times, and steady-state currents along with enhanced sensitivity due to mass transport by radial diffusion (Wightman 1981, Wehmeyer and Wightman 1985, Wojciechowski and Balcerzak 1990, Fungaro and Brett 1999). This enhanced sensitivity has led to applications for trace and ultratrace level analysis of metal cations in a large variety of solutions and volumes. The small size also allows for the development of electrode arrays that can further increase measurement sensitivity.

Some observations from these studies involving microelectrodes include validation of one proposed mechanism for Ln reduction at a mercury film using a mercury film microelectrode (Schumacher et al. 2011c). Others include the quantitative determination of Ln with an Au microelectrode, the examination of current changes due to adsorption at high scan rates (Pourjavid et al. 2009a,b), and the development of an electrochemical flow-through cell for rapid analysis of heavy elements using a Nafion-coated

carbon fiber (Toyoshima et al. 2008). The flow-through cell was validated with 10^{10} Ce^{3+}/Ce^{4+} atoms in solution. Lastly, the development of a Lu^{3+} microsensor that exhibited characteristics similar to previously discussed ISEs (Ganjali et al. 2009, 2010, Norouzi et al. 2010), with the LOD lowered by two orders of magnitude and the validation of sensor operation in aqueous and binary solutions (Ganjali et al. 2007).

The unique characteristics of microelectrodes facilitate detailed investigations into mechanisms and electrochemical properties of Ln and An that are not easily obtained with conventionally sized electrodes. Using a microelectrode allows the researcher to operate in small volumes with enhanced sensitivity providing a wider array of experiments with radionuclides at lower concentration levels and in a larger variety of solution compositions. Conversely, operating at low levels requires a much larger emphasis on minimizing sample contamination; however, the benefits outweigh the effort required. The ability to incorporate a microelectrode electrochemical detector to a separation technique as discussed by Toyoshima et al. (2008) and Pourjavid et al. (2009a,b) has numerous potential applications within the field.

Although electrochemical detection is already widely used for separation instruments, microelectrodes provide for more rapid analysis with higher sensitivity and could prove potentially useful in examining the redox properties of shorter-lived radionuclides where relatively small amounts of material are produced. Implied in the previous statement is the understanding that a method exists to transfer the radionuclides from a production chamber to an electroanalytical apparatus. Toyoshima et al. (2008) provides a good starting description of how such an apparatus might operate.

Electrochemical studies in nonaqueous and mixed solvent solutions

A modest amount of research has been conducted on the electrochemical properties of Ln and An in nonaqueous solvents as a result of developing new methods for the reprocessing of spent nuclear fuels (Martinot et al. 1990) and in mitigating the large background signal from H$_3$O$^+$ reduction (Chlistunoff and Galus 1985). Although one drawback to nonaqueous solvents is the lack of solubility of inorganic cations in organic solvents, one of the greatest inherent advantages is the expansion of the

electrochemical window, which can easily reach 5.0 V in the case of hexamethylphosphoramine (Martinot et al. 1990). Table 6 lists the variation in solutions and the observed reduction potentials. When compared with the previous tables, a clear shift in potentials is observed. Choosing a nonaqueous solvent requires a balance between a high enough donor number to allow the properties of the solvent to be compared from the standpoint of ion solvation (Elzanowska et al. 1983) while ensuring that shift in cathodic potential does not exceed the solvent limit.

One advantage to working in nonaqueous media is the observed potential shift. Elzanowska et al. (1983) suggested that the donor number is directly correlated to the shift. The larger donor number correlated with an increase in reorganization energy (λ). The activation energy for reduction is increased as a result of the increased λ and larger potentials are necessary for the reduction of Ln and An. Many others have observed this shift in their work (Gao and Guan 1988, Martinot et al. 1990). One study by Chlistunoff and Galus (1985) found that the addition of DMF to an aqueous solution resulted in a cathodic shift, with slight alterations in slope and shape of Eu voltammograms. Although the addition of a non-aqueous solvent altered the voltammograms by changing solution conditions, Trubachev (2003) suggested that the correlation between the donor and the coordination number and redox shifts could be used to predict changes in specified solution conditions.

Besides shifting the redox potentials of Ln and An, nonaqueous solvents have been shown to support the presence of oxidation states not normally observed under aqueous conditions. The presence of these species has been attributed to the complexation with either the nonaqueous solvent itself or with an added complexing ligand. Gao and Guan (1988) found that addition of 18-Crown-6 produced a greater stability of the Eu^{2+} state. Another example is the disproportion of U(V), which readily occurs in an aqueous solution is stabilized in organic solvents and leads to a decrease in the rates of reaction (Martinot et al. 1992, Suzuki et al. 2007). Other work citing this phenomenon with uranium include discussions on kinetic parameters and changes in pH or acid (Martinot et al. 1992, 2002, Suzuki et al. 2007, Elkechai et al. 2009).

Alternative f-element oxidation states

A majority of An can exhibit stable oxidation states different from the expected trivalent state of Ln with the exception of Eu and Ce. Although other states are possible, only a few are commonly observed. Trivalent states are common for Ac, Am, Cm, Bk, Cf, Es, Fm, Md, and Lr in aqueous solution, whereas the tetravalent state is common for Th, U, and Pu. Other An, such as Pa, U, Np, and No, can be stable in aqueous solutions in higher or lower oxidation states (Cotton 2006). The less common oxidation states can be observed experimentally under the specified conditions. Radiopolarographic studies performed in aqueous media observed slopes above the expected 20 mV for Fm, suggesting a mechanism that exchanges two electrons per mole, leading to the identification of divalent Fm as a stable oxidation state (Samhoun and David 1979). Similarly, divalent Md was identified by slope analysis (David et al. 1981).

Table 6 Summary of electrochemical data of Ln and An in nonaqueous solution.

Metal	E (V)[a]	Background electrolyte	Mechanism	Temperature (°C)	Electrode	References
Ce	-1.752	BMIM Cl	3 to 0	70	Pt	Rao et al. 2010
Sm	-1.41	BMIM Cl	3 to 0	70	Pt	Rao et al. 2010
Eu	-0.3	EMITFSI	3 to 2	25	GCE	Yamagata et al. 2006
Eu	-0.269	BMPTFSI	3 to 2	25	GCE	Yamagata et al. 2006
Eu	-1.762	BMIM Cl	3 to 2	70	Pt	Rao et al. 2010
Yb	-0.993	BMPTFSI	3 to 2	25	GCE	Yamagata et al. 2006
Th	-1.8	[(n-C_4H_9)(CH_3)$_3$N]-[Tf_2N]	4 to 0	25	GCE	Binnenmans 2007
Tb	-2.359	LiCl-KCl eutectic	4 to 0	450	GCE	Binnenmans 2007
U	-1.481	NaCl-2CsCl	4 to 3	650	GCE	Nagai et al. 2005

[a]Potentials are temperature dependent.

To confirm the existence of alternate oxidation states in solution, complexing agents and/or alternative non-aqueous medium can be used. David et al. (1981) confirmed the divalent state of Fm by citrate complexation. In the presence of citrate, the half-wave potentials of Fm are shifted similarly to Mn^{2+}-citrate complexation, increasing the likelihood of the Fm divalent state. Additionally, the differences between a trivalent and divalent citrate complex can be discerned based on the ion's affinity for complexation. Besides complexation with a ligand, the interactions of these metals in non-aqueous media can stabilize alternative oxidation states. Uranium metal can be observed from electrochemical reduction in γ-BL/THF (Martinot et al. 2002). The oxidation of U(III) to (IV) and (IV) to (V) was observed in THF and Bu_4NPF_6 with a platinum electrode. Although the oxidation was reversible, the evidence of the existence of the (V) state was detected (Elkechai et al. 2009). The U(V) state was also observable in perchloric acid solution and noticeably stable in the presence of malonic and oxalic acid (Suzuki et al. 2007). Lastly, working in nonaqueous solutions allows for a greater potential window, which allows for the more negative reduction potentials to be attained, increasing the accessibility of alternative An oxidation states (Cotton 2006).

Stabilizing and observing less common An oxidation states can also be done with alternative analytical techniques. For environmental samples, oxidation states can be determined by ion chromatography (Coates et al. 2001). In a few cases, certain oxidation states cannot be differentiated, particularly if the matrix conditions do not support one state. An and Ln compounds in unusual oxidation states can also be formed through specified synthetic routes. The use of superoxidizers and superacids has been shown to produce Pu(VI) and Pr(IV) compounds, and oxidation states of VI, V, IV, and III have been stabilized for multiple An in perovskite complexes (Eller and Penneman 1987). In general, the higher and lower uncommon oxidation states can be stabilized in cubic complexes or polymer-type structures, such as ternary oxides, binary oxides, binary fluorides, and oxyfluorides (Eller and Penneman 1987).

Conclusion

Since the mid-1980s, much progress has been made on determining the electrochemical properties of Ln and An in both aqueous and nonaqueous solutions. In both solvents, large negative potentials are required to reduce these elements to their metallic state. These electrochemical properties are susceptible to variances in the solution conditions that need to be carefully controlled. Because of the similarity of electrochemical properties, the separation and detection of individual Ln and An within a mixture are difficult to achieve solely by electroanalytical techniques; however, advances in technology have facilitated the development of separations in some circumstances when combining electroanalytical techniques with other separation techniques. CP electrodes represent a very appealing avenue to pursue in terms of pre-concentration, individual detection and/or separation within a mixture due to their ease of modification, and the large variety of ligands that can be incorporated into the paste. Advances in microelectrode technology allow for electrochemical analysis on a per-atom basis, which provide promise in furthering separation and detection research regarding Ln and An. It will be interesting to see what advances are made within the fields of radiochemistry and electroanalytical chemistry as technology and knowledge increase.

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