Environmental benefits of methanesulfonic acid:

Comparative properties and advantages

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Summary

This paper reviews some chemical and physical characteristics of methanesulfonic acid and the short-chain alkanesulfonic acids in general. The aqueous solubility of metal methanesulfonates, the conductivity of aqueous methanesulfonic acid (MSA) solutions and the low toxicity of MSA all make MSA(aq) an ideal electrolyte for many electrochemical processes, especially those involving tin and lead. Aspects of aqueous process effluent treatment, acid recovery and metal alkanesulfonate salt preparation are also environmentally favorable. Emphasis in this paper is given to rationalizing the rapidly growing commercial preference for MSA(aq) as an electrochemical electrolyte, especially with respect to the substitution of MSA for HBF_4 in the electroplating of Sn/Pb solder. Economic aspects of MSA are also considered.

Introduction

Methanesulfonic acid is the commercial electrolyte standard for the electroplating of Sn/Pb solder, and over the past 20 years MSA has largely replaced fluoroboric acid, the previous industrial standard, as the electrolyte of choice for electrochemical processes involving lead. MSA is also an emerging electrolyte choice for the electroplating of pure tin on sheet steel. The wide acceptance of methanesulfonic acid (MSA) as an acid electrolyte for electrochemical processes, especially those involving tin and lead, has resulted from a combination of diverse physical and chemical properties. These properties include high saturation metal salt solubilities, high conductivity, ease of effluent treatment and low relative toxicity. A full understanding of the functional and environmental benefits of MSA requires a simultaneous appreciation of several distinctly different subject areas. The authors have over the past 10 years developed a significant body of data related to a number of commercially significant aspects of MSA, and in this paper we have endeavored to present those properties of MSA which make it an advantageous electrolyte. This paper is not intended as a comprehensive review of the uses and/or properties of MSA, but rather it is intended to offer a reasonable explanation, largely based on work conducted at Elf Atochem, as to why MSA has become the electrolyte of choice in a number of electrochemical applications.

Criteria for selection of acidic electrolytes for electrochemistry

Electroplating processes typically involve the electrolytic deposition of a thin coating of a metal onto a conductive substrate.[1] Such processes are normally carried out in ionically conductive aqueous solutions, and such aqueous solutions are normally made conductive by the addition of acids, bases and/or neutral salts. In general, plating processes are classified according to the nature of the aqueous electrolyte (acid, base, neutral) employed. Acid based electrolytes are desirable in that they allow for very high solution conductivity and metal ion solubility. Consequently, a number of commercial electroplating processes (*e.g.*, Ferrostan™, Ronastan™, Techni Solder™, Solderon™, *etc.*) have adopted standard acid electrolytes.[1–3]

Certain metal salts, such as those of Cu, Ni and Sn, are soluble in most acid electrolytes (*e.g.*, H_2SO_4, HCl, HBF_4, $MeSO_3H$, *etc.*), and solubility considerations are not important in the selection of acid electrolytes for electroplating process involving such metals. Other metal salts, such as those of Pb and Ag, are only soluble in a limited number of acid electrolytes, and solubility considerations are paramount in the design of acid electrolytes for such metals. The high aqueous solubilities of metal salts of MSA make it an ideal electroplating electrolyte. The solubility advantage is particularly great for Sn(II), Hg(II), Pb(II) and Ag(I) salts. The saturation solubilities of some metal methanesulfonates (compounds **1**–**18**, preparative details are included in the Experimental section, listed in ascending order in Table 1), metal sulfates and metal chlorides are presented in Table 1.

Table 1 clearly shows the high solubility of the Ca(II), Sr(II), Ba(II), Ag(I), Sn(II), Pb(II) and Hg(II) salts of MSA relative to the corresponding salts of sulfuric acid. Also, the high solubility of the Ag(I), Pb(II) and Hg(II) salts of MSA relative to the corresponding salts of hydrochloric acid is clearly seen. The universal aqueous solubility of metal salts of MSA is similar to the

Green Context

The electroplating industry is a major user of chemicals. One concern which has been growing in the last few years is the use of acid electrolytes. This paper discusses the benefits to be gained from the use of methanesulfonic acid in electrochemical processes involving lead and tin. Effluent treatment, acid recovery and salt formation are all aspects of the process as a whole where the use of methanesulfonic acid is of environmental benefit. ***DJM***

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Table 1 The aqueous saturation solubility of some metal methanesulfonates, chlorides and sulfates at room temperature (22 °C)

Metal cation[a]	Aqueous saturation solubility (mol dm^{-3} as metal)[b] Methanesulfonate	Sulfate	Chloride
NH_4^+	6.83	8.17	5.06
Li^+	7.06	4.90	9.37
Na^+	5.65	2.78	5.57
K^+	4.48	1.25	3.86
Mg^{2+}	1.40	2.63	5.02
Ca^{2+}	2.92	0.0249	5.51
Sr^{2+}	2.55	0	3.04
Ba^{2+}	1.59	0	1.71
Mn^{2+}	2.90	3.52	4.12
Co^{2+}	2.53	2.16	3.87
Ni^{2+}	2.13	2.44	4.38
Cu^{2+}	2.00	1.35	4.87
Ag^+	3.72	0.0556	0
Zn^{2+}	2.16	3.32	13.0
Cd^{2+}	3.20	3.10	5.71
Sn^{2+}	3.73	1.42	4.91
Hg^{2+}	1.81	0	0.239
Pb^{2+}	2.60	0	0.0338

[a] Preparations of the metal methanesulfonates (compounds **1**–**18**) are given in the Experimental section. [b] All measurements were made at Elf Atochem's King of Prussia Technical Center (see Experimental section).

universal aqueous solubility of metal salts of nitric acid and perchloric acid, but, as is shown throughout this article, MSA also offers a significant number of other advantages in addition to this universal aqueous metal salt solubility.

Some pertinent properties of methanesulfonic acid

The utility of methanesulfonic acid (MSA) in numerous application areas (esterification catalysts, alkylation catalysts, polymer solvents, electroplating, electrochemistry, *etc.*) derives from a number of physical and chemical properties which in combination are unique. For instance, MSA(aq) allows for excellent solubilization of metal salts and surface active agents. MSA has a low tendency to oxidize organic compounds. MSA is a strong acid ($pK_a = -1.9$)[4] which is almost completely ionized at 0.1 M in aqueous solution.[4] MSA(aq) solutions exposed to open atmospheric conditions display a unique stabilization of metal ions in their lower valence states, or, stated differently, MSA solutions allow for a unique resistance to the oxidation of metal ions to their higher valent states. This oxidative stability of metal ions in MSA(aq) solutions is perhaps best known for the Sn(II)/Sn(IV) system. Of all the common acid electrolytes, MSA based aqueous solutions of Sn(II) have displayed the highest stability known toward oxidation to Sn(IV).[5] The oxidation of tin(II) to tin(IV) causes an insoluble stannic sludge to form in the electrolyte, and such sludge is difficult to remove and waste-treat.

Comparative toxicity and environmental properties of MSA

The 'green' character of methanesulfonic acid, especially as compared to fluoroboric acid and fluorosilicic acid, is derived from several factors. In general, MSA is less toxic than fluoroboric acid and fluorosilicic acid. Fluoroboric acid has a reported LD_{50} (oral, rat) of 464–495 mg kg^{-1}, while MSA has a reported LD_{50} (oral, rat) of 1158 mg kg^{-1}.[6] In addition, fluoroboric acid and fluorosilicic acids have lachrymatory properties, and both acids can evolve HF. As a result of their tendency to evolve HF, fluoroboric acid and fluorosilicic acid have established OSHA PEL (permissible exposure limit) levels of 2.5 mg HF per cubic meter (8 h, TWA).[7] It has been found that HF levels in excess of the OSHA PEL can develop in the atmosphere surrounding fluoroboric acid and fluorosilicic acid solutions when ventilation is inadequate.[8] MSA has no established OSHA PEL, as MSA(aq) solutions do not, under normal conditions, evolve any dangerous volatile chemicals. In general, the low toxicity of MSA, especially when compared to HF complex acids like fluoroboric acid and fluorosilicic acid, makes it a safe electrolyte to handle.

MSA is considered readily biodegradable (OECD 303A, OECD 301D closed bottle, OECD 301A DOC Die-Away, BOD), ultimately forming sulfate and carbon dioxide. In fact, MSA is considered to be a natural product, and MSA is part of the natural sulfur cycle.[9] By contrast, discharged fluoroboric acid undergoes hydrolytic dissociation into boric acid and fluoride while discharged fluorosilicic acid undergoes hydrolytic dissociation into silicic acid (silica) and fluoride. In the case of fluoroboric acid, both fluoride and boron are environmentally troublesome, while for fluorosilicic acid, the fluoride is a problem. In general, the benign nature of MSA, especially when compared to HF complex acids like fluoroboric acid and fluorosilicic acid, makes it an environmentally advantageous electrolyte.

Comparative conductivity of methanesulfonic acid

Electrolyte conductivity is an important parameter in electroplating. Higher electrolyte conductivity leads to lower overall cell voltage, and a minimal cell voltage leads to a minimal electricity cost. The electrical cost of any electrochemical process can be given by the formula $EC = 3600\,kVI$ (EC = electrical cost of the process per hour, k = utility cost per joule, V = cell voltage in volts, I = cell current in amperes). Usually, the current is set equal to $(A_E)(CD_O)$, where A_E is the total electrode area and CD_O is the optimal current density for the process, and the utility cost is fixed by market conditions. Thus, minimizing electrical cost is tantamount to minimizing cell voltage, and one good way to minimize cell voltage is to maximize electrolyte conductivity. Note that saving money by consuming less electricity is both economically and environmentally beneficial. The environmental benefit derives from the consequent reduction in the use of fuel by the electricity generating utility company.

For comparison purposes, the equivalent conductance of 2, 1, 0.5, 0.1, 0.05 and 0.01 N aqueous solutions of H_2SO_4, HCl, $MeSO_3H$, $EtSO_3H$ and Pr^nSO_3H are given in Table 2.

The conductivity behavior of methanesulfonic acid (MSA), ethanesulfonic acid (ESA) and propanesulfonic acid (PSA) can be seen to be comparable to the conductivity behavior of other strong acids such as sulfuric acid and hydrochloric acid. While the conductivity displayed by MSA(aq) is not exceptional with respect to other strong acids, it is, in combination with MSA's other beneficial properties, another piece in the puzzle that explains the ever increasing commercial adoption of MSA(aq) as an electrolyte for electrochemical processes.

A Kohlrausch plot of the conductivity data given in Table 2 is presented in Fig. 1. The Kohlrausch plot allows for better visualization of the conductivity data. One interesting observation from the plot is the increased equivalent conductivity of MSA(aq) over H_2SO_4(aq) in the acid concentration range from 0.01 to 2 N.

Table 2 The equivalent conductance of aqueous solutions of some commonly available acids. Equivalent conductance values are reported in S cm^2 mol^{-1}

Acid	2 N	1 N	0.5 N	0.1 N	0.05 N	0.01 N
Hydrochloric	—	346.11	373.53	403.63	412.12	421.80
Sulfuric	413.84	444.88	464.12	529.08	572.76	699.40
Methanesulfonic	232.97	299.60	336.47	372.74	381.76	391.78
Ethanesulfonic	200.30	276.95	320.79	364.36	373.27	384.16
Propanesulfonic	187.96	268.06	314.88	361.26	370.65	382.20

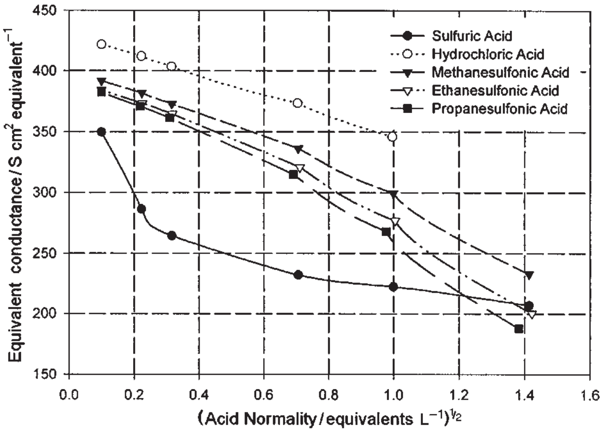

Fig. 1 A Kohlrausch plot of conductivity data for H_2SO_4(aq), HCl(aq), MSA(aq), ESA(aq) and PSA(aq). The conductivity values are also tabulated in Table 2.

Recovery of methanesulfonic acid from commercial processes

An electrowinning acid recovery method (designated by acronym as EWARE) which allows for the recovery of pure alkanesulfonic acids (*e.g.*, MSA) from corresponding metal alkanesulfonate salts has been developed. The process is based on electrowinning out of an anion-exchange membrane divided cell. The anode process is O_2/H^+ generation, and the cathode process is metal electrodeposition. The process is shown schematically in Fig. 2.

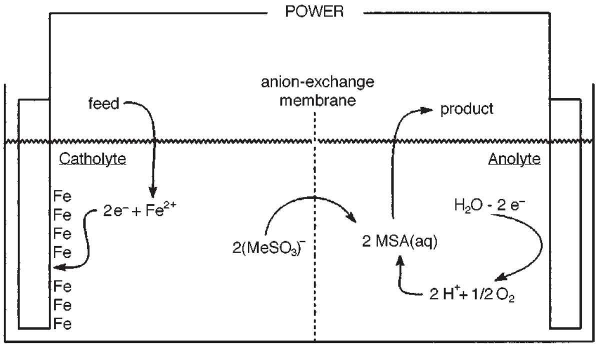

Fig. 2 Divided cell electrowinning for the recovery of MSA from $Fe(O_3SMe)_2$.

In Fig. 2, iron electrodeposition is the cathode process, O_2/H^+ generation is the anode process and methanesulfonate transport is the anion-exchange membrane process. The reduction of water to hydrogen and hydroxide competes with iron deposition at the cathode, but this competitive process does not necessarily reduce the efficiency of the acid recovery process. Only proton backleakage through the anion-exchange membrane reduces the overall efficiency of acid recovery. However, when the reduction of water becomes a significant portion of the overall cathode reaction, then metal oxide sludging, as opposed to metal electrodeposition, becomes the dominant catholyte process.

While conceptually similar processes are available for fluoroborate and/or fluorosilicate based electrolytes, there are a number of practical problems which plague systems designed to recover HBF_4 and H_2SiF_6 from waste streams. HBF_4 and H_2SiF_6 tend to dissociate into BF_3/HF and SiF_4/HF respectively, during transport through anion-exchange membranes. Such dissociation results in the formation of more mobile fluoride anions as compared to the bulkier fluoroborate and/or fluorosilicate anions. In addition, fluoroborate and fluorosilicate undergo hydrolysis reactions in alkaline solution, and acid recovery catholyte solutions often become alkaline during the recovery process. All things considered, the recovery of MSA from metal alkanesulfonate based waste is easier than the recovery of HBF_4 or H_2SiF_6 from metal fluoroborate and metal fluorosilicate waste, respectively.

The EWARE process can also be conducted in an undivided electrowinning cell operated in batch mode, but the use of an undivided cell often results in low collection efficiency and poor product quality. In the recovery of acid value from iron, cobalt and nickel salts (first row Group VIII transition metals), the performance of an undivided electrowinning cell is particularly poor (see electrowinning procedure 1 in the Experimental section). This is due to the low efficiency of electrodeposition of first row Group VIII metals from acidic solutions. Industrial waste solutions containing iron, nickel and/or cobalt salts are often slightly acidic, and a good recovery technique must be capable of recovering acid value from such acidic waste solutions. The anion-exchange membrane divided cell works well here because it allows for an initial increase of the waste stream pH (by cathodic base generation) up to a value at which metal deposition becomes practical. Once metal deposition begins, the pH increase is halted. Thus, the process is ‘self-stabilizing’ in nature. In the early stages of acid recovery by electrowinning from a solution of Fe, Co and/or Ni salts, very little metal is actually deposited on the cathode. Instead, base is produced on the cathode while acid is produced on the anode. The net result of the divided cell electrowinning process during this early stage is simply movement of acid from the cathode compartment to the anode compartment. After sufficient acid has been moved from the catholyte into the anolyte, the depositon of Fe, Co and/or Ni begins. While the use of an undivided cell is possible for waste streams which do not contain Fe, Co or Ni salts, it is generally better to use a divided cell process for all waste streams. The divided cell process allows for the recovery of pure acid with <10 ppm of metal contamination, while the use of an undivided cell produces acid with much higher residual metal contamination (see electrowinning procedure 1 in the Experimental section).

Anion-exchange membranes are thin sheets of polymeric material wherein the polymer structure contains fixed ammonium and/or amine groups distributed throughout the backbone. Furthermore, these anion exchanging ammonium groups are at least partially distributed in porous channels dispersed throughout the membranes structure. These porous channels are of molecular dimensions, and they are responsible for the selective transport of anions. For a more thorough discussion of ion permeable membranes see, for instance; T. A. Davis, J. D. Genders and D. Pletcher, *A First Course in Ion Permeable Membranes*, Alresford Press Ltd., UK, 1997. It is known that anion-exchange membranes have, under certain conditions, restricted stability and longevity. In particular, anion-exchange membranes are susceptible to chemical degradation in the presence of strong bases and oxidizing agents. Strong oxidants cause damage *via* oxidation of the amine/ammonium groups to amine oxides while strong bases cause damage *via* Hofmann type eliminations of amines from the polymer backbone. In the application discussed here, the anion-exchange membrane is not exposed to strong bases or oxidants. Thus, the average longevity of anion-exchange membranes in this application is equal to or greater than the average life of other durable membrane materials such as Nafion.

The divided cell process was optimized for use with both continuous anolyte and catholyte streams. The catholyte stream was an aqueous solution of a metal alkanesulfonate salt. In continuous mode, the catholyte stream was continuously recycled while being maintained at constant metal salt concentration by additions of solid salt and/or concentrate. The anolyte stream contained the generated alkanesulfonic acid product. In continuous mode, the anolyte stream was continuously removed while anolyte volume was made-up with deionized water. Cathodic metal deposits were removed on a regular schedule.

Continuous electrowinning was found useful for the recovery of pure alkanesulfonic acids from solutions of relatively pure metal alkanesulfonate salts. Alternatively, the same continuous electrowinning process could be used for the recovery of less pure acid from old, contaminated and/or off-specification alkanesulfonic acid based solutions containing dissolved metals, surfactants, organics, *etc.* (*e.g.*, electroplating solutions).[10] In some cases, the best results were obtained by the initial removal and partial purification of a metal alkanesulfonate salt prior to acid recovery. The removal and isolation of relatively pure metal alkanesulfonate salts from commercial solutions (*e.g.*, electroplating solutions) can be achieved *via* numerous methods including ion-exchange, selective crystallization and/or evaporation.

An application of particular importance involves alkanesulfonic acid recovery from iron(II) methanesulfonate. Iron(II) methanesulfonate is a by-product of iron removal from contaminated MSA-based strip steel tinplate solutions. The iron is removed by cooling the iron contaminated solutions followed by precipitation of iron(II) methanesulfonate. Iron contamination in acid tinplate solutions results from the unavoidable corrosion of the steel strip being plated. The dissolved iron introduced by corrosion catalyzes the air oxidation of tin(II) to tin(IV), with precipitation of tin(IV) from the tinplate solution as sludge. In order to minimize sludge formation, dissolved iron must be continuously removed. The removal of iron(II) methanesulfonate from MSA based acid tinplate solutions results in a loss of significant MSA value, and MSA recovery from the segregated iron(II) methanesulfonate is necessary for economic reasons. Both ion-exchange and continuous electrowinning processes can be used to recover MSA from iron(II) methanesulfonate, but continuous electrowinning is less difficult and provides for a purer product.

The use of electrowinning for the removal of metal ions from commercial effluent solutions and/or for the recovery of metal value from commercial leach solutions is well known. In environmental waste treatment applications, the process is optimized for the reduction of metal levels in effluent solutions. In commercial metal refining and recovery applications, the process is optimized for the production of pure metal. Additionally in many commercial refinery operations (*e.g.*, electrowinning of Zn), the recovery of impure acid for reuse as a leachant is also an important part of the overall process economics. Electrowinning in an anion-exchange membrane divided cell with both continuous anolyte and catholyte feeds, as described herein, is optimal for the generation of substantially pure acid for general reuse. The quality of the alkanesulfonic acid produced by the EWARE continuous electrowinning process is equivalent to the quality of the same alkanesulfonic acid as provided commercially by primary producers.

It is also possible to use continuous, divided cell electrowinning as part of a primary process for the manufacture of organic sulfonic acids. The oxidation of lead mercaptide compounds to lead alkanesulfonates with nitric acid has been reported.[11] Previous workers have converted such lead alkanesulfonates to free alkanesulfonic acid *via* precipitation of lead chloride following treatment with HCl. One could also use the electrowinning process described herein for the ultimate production of free alkanesulfonic acids (M = divalent metal cation), as shown in eqns. (1a) and (1b).[12]

$$(\mathrm{RS})_2\mathrm{M} + 3\ \mathrm{O}_2 \longrightarrow (\mathrm{RSO}_3)_2\mathrm{M} \qquad (1a)$$

$$(\mathrm{RSO}_3)_2\mathrm{M} + \mathrm{H}_2\mathrm{O} \longrightarrow \mathrm{M} + 2\ \mathrm{RSO}_3\mathrm{H} + 1/2\ \mathrm{O}_2\ (\text{electrowinning}) \qquad (1b)$$

Industrial production of fluoroboric acid, fluorosilicic acid and MSA

Fluoroboric acid is produced by the reaction of HF with boric acid, as shown in eqn. (2).[13]

$$4\ \mathrm{HF} + \mathrm{H}_3\mathrm{BO}_3 \longrightarrow \mathrm{HBF}_4 + 3\ \mathrm{H}_2\mathrm{O} \qquad (2)$$

The acid is typically sold as a 48% aqueous solution. The major markets for fluoroboric acid are as a plating electrolyte and as a raw material in the manufacture of fluoroborate salts. Iron(II) fluoroborate and lead(II) fluoroborate are produced for use in fluoroborate based Sn/Pb solder electroplating solutions. Potassium fluoroborate is produced for use in the preparation of aluminium master alloys. The preparation and use of fluoroboric acid and fluoroborate salts is hindered by the high toxicity of HF. Aqueous solutions containing HBF_4 tend to emit HF into the atmosphere surrounding them. Such HF emission can be diminished by the addition of boric acid, but low levels of HF in the work area can not be avoided.

Fluorosilicic acid can be produced by the reaction of HF with silica, as shown in eqn. (3).[14]

$$6\ \mathrm{HF} + \mathrm{H}_2\mathrm{SiO}_3 \longrightarrow \mathrm{H}_2\mathrm{SiF}_6 + 3\ \mathrm{H}_2\mathrm{O} \qquad (3)$$

More commonly, fluorosilicic acid is obtained as a by-product of fluorophosphate mineral based production of phosphoric acid, as shown in eqn. (4).[14]

$$2[\mathrm{Ca}_3(\mathrm{PO}_4)_2\cdot\mathrm{CaF}_2] + 8\ \mathrm{H}_2\mathrm{SO}_4 + 16\ \mathrm{H}_2\mathrm{O} \longrightarrow 8\ \mathrm{CaSO}_4\cdot 2\ \mathrm{H}_2\mathrm{O} + 4\ \mathrm{H}_3\mathrm{PO}_4 + 4\ \mathrm{HF} \qquad (4)$$

The HF produced *via* the above process reacts with silica also present in the mineral to produce a by-product stream of fluorosilicic acid. Anhydrous fluorosilicic acid dissociates almost instantaneously into SiF_4 and HF. At 19 °C and at aqueous concentrations between 60 and 70% by weight, fluorosilicic acid crystallizes as the dihydrate. Fluorosilicic acid is typically sold as a 25% aqueous solution. A major market for fluorosilicic acid is as a fluoridation agent for municipal water supplies. Other markets include lead refining and fluorosilicate salt manufacture. As with fluoroboric acid, the preparation and use of fluorosilicic acid and fluorosilicate salts is hindered by the high toxicity of HF.

Aqueous solutions containing H_2SiF_6, as for HBF_4(aq), continuously emit HF into the atmosphere surrounding them.

The development of commercial processes for the preparation of C_1 through to C_4 alkanesulfonic acids began in the 1940s with the work of Wayne Proell (Standard Oil of Indiana).[15] Proell's preparative method employed an initial NO_x catalyzed air oxidation of an alkyl mercaptan followed by a secondary stripping procedure which removed residual NO_x from the sulfonic acid product, as shown in eqn. (5).

$$2\ MeSH + 3\ O_2 \rightarrow 2\ MeSO_3H \qquad (5)$$

Proell also developed a number of applications of alkanesulfonic acids as alkylation catalysts,[16] as intermediates in the direct formation of sulfonate esters by reaction with olefins[17] and as electroplating electrolytes[18] with emphasis on copper plating.[19] Proell's early work in the field of sulfonic acid technology was both inspired and prolific, but his contributions were ahead of their time. It would not be until the early 1980s that a significant market for alkanesulfonic acids developed, and the first major customers turned out to be electronic components producers (*e.g.*, Intel, Motorola, AMD) who used MSA(aq) as an electrolyte for Sn/Pb solder electroplating.

The production of sulfonic acids by the air oxidation of mercaptans has the advantage of a very inexpensive oxidant (air), but the method suffers from several practical problems including poor product quality and the potential for explosions. The first practical short-chain alkanesulfonic acid preparation was developed by Pennwalt Corporation in 1967 (Pennwalt Corporation became part of Elf Atochem in 1989).[20] The Pennwalt method employed the direct chlorine oxidation of an aqueous emulsion of a mercaptan, as shown in eqn. (6).

$$RSH + 3\ Cl_2 + 3\ H_2O \rightarrow RSO_3H + 6\ HCl \qquad (6)$$

Several sulfonic acid preparations *via* anodic oxidation of mercaptans and/or disulfides have also been developed, but to date the economics have been prohibitive. Atochem has developed and patented a useful method for producing dialkanesulfonyl peroxides *via* the anodic oxidation of anhydrous alkanesulfonic acids.[21]

MSA in electrochemical processes involving lead

The design of acid electrolytes for the electroplating of Pb and Pb alloys, most importantly Sn/Pb, is dominated by solubility, performance and environmental considerations. Two important modern technologies depend integrally on the aqueous electrochemistry of lead; these are the electrodeposition of Sn/Pb solder in the electronics industry and the production of Pb acid batteries for the automotive industry. In addition, the refining of crude Pb obtained from mining and/or recycling operations is sometimes carried out electrolytically. As of today, only fluoroboric acid, fluorosilicic acid and methanesulfonic acid based electrolytes have been used with commercial success.[22,23]

Methanesulfonic acid is functionally and environmentally superior to fluoroboric acid (HBF_4), fluorosilicic acid (H_2SiF_6) and other HF complex acids (*e.g.*, HPF_6, $HSbF_6$) as an electrolyte for electrochemical processing. The advantages of MSA are evidenced by the recent (starting in about 1980 and continuing to today) substitution of MSA for HBF_4 in the commercially important electroplating of Sn/Pb solder. In this process, acidic aqueous solutions of Sn(II), Pb(II), free acid and surface active additives are employed. From these carefully formulated MSA based electroplating solutions, it is possible to produce solderable Sn/Pb coatings with specific properties (appearance, alloy content, thickness, ductility, *etc.*). Such engineered Sn/Pb coatings are, for example, deposited on the connecting pins of electrical devices, where they function to, among other things, protect the connecting pins from oxidation and the associated loss of solderability. Solderable Sn/Pb coatings are also sometimes electroplated onto printed circuit boards as part of the fabrication process, and Sn or Sn/Pb is electroplated onto wire as a solderable and corrosion inhibiting coating. A number of industrial electrochemical processes still employ fluoroboric and/or fluorosilicic acid based electrolytes. For many of these applications, active research programs aimed at replacing the HF complex acid with MSA are in place. In the electrorefining of lead, for instance, crude lead bullion anodes contained in an undivided electrochemical cell are electrolytically dissolved into and simultaneously cathodically redeposited, in purer form, from fluorosilicic acid based electrolytes. The substitution of MSA for fluorosilicic acid in the electrorefining of lead offers a number of functional and environmental advantages.[24] In both Sn/Pb solder electroplating and lead electrorefining, acidic aqueous solutions with a high concentration of Pb(II) ions are required.

Only certain acid electrolytes will allow for a high aqueous solubility of Pb(II) ions. These electrolytes include methanesulfonic acid (MSA, $MeSO_3H$), fluoroboric acid (HBF_4), fluorosilicic acid (H_2SiF_6), nitric acid (HNO_3), perchloric acid ($HClO_4$), chloric acid ($HClO_3$), acetic acid ($MeCO_2H$) and dithionic acid ($H_2S_2O_6$). The aqueous saturation solubilities of the relevant lead salts are shown in Table 3.

Table 3 Saturation solubility of some lead salts; temperature and solubility units in parentheses

Lead salt	Aqueous saturation solubility
Methanesulfonate, $Pb(O_3SMe)_2$	143 g per 100 g H_2O (25 °C)[a]
Fluoroborate, $Pb(BF_4)_2$	50 wt.% (20 °C)[b]
Fluorosilicate, $PbSiF_6 \cdot 4H_2O$	69 wt.% (20 °C)[c]
Nitrate, $Pb(NO_3)_2$	37 wt.% (25 °C)[d]
Perchlorate, $Pb(ClO_4)_2$	226 g per 100 g H_2O, 25 °C)[e]
Chlorate, $Pb(ClO_3)_2$	255 g per 100 g H_2O (25 °C)[f]
Acetate, $Pb(O_2CMe_3)_2$	55 g per 100 g H_2O (25 °C)[g]
Dithionate, $PbS_2O_6 \cdot 4H_2O$	115 g per 100 g H_2O (20 °C)[h]

[a] *MSA In Electrochemical Applications, Elf Atochem Technical Bulletin A-70-6*, 1991, p. 5. [b] Measurement made by Fidelity Chemicals Corporation of Newark, NJ, USA. [c] J. A. Gonzalez, PhD Thesis, University of British Columbia, *Electrochemical Processes Within the Slimes Layer of Lead Anodes During Betts Electrorefining*, 1991, p. 334. From: *Diss. Abstr. Int. B*, 1993, **53**, 4885. [d] A. A. Kazantsez, *Russ. J. Inorg. Chem.*, 1960, **5**, 773. [e] H. H. Willard and J. L. Kassner, *J. Am. Chem. Soc.*, 1930, **52**, 2391. [f] *Gmelin Handbuch der Anorganischen Chemie; Volume Pb*, 1969, vol. 1, p. 34. [g] M. L. Dundon and W. E. Henderson, *J. Am. Chem. Soc.*, 1922, **44**, 1196. [h] *CRC Handbook*, ed. R. Weast, Boca Raton, FL, 68th edn., 1987, p. B-101.

Various factors make the use of many of these 'solubility permissible' lead electrolytes untenable. For instance, the dithionate anion in lead dithionate is unstable at low pH, decomposing into sulfate and sulfite. Aqueous solutions of lead acetate in combination with acetic acid have insufficient conductivity to allow for high-speed electroplating operations. Lead chlorate, lead perchlorate and lead nitrate all tend to decompose cathodically, and the corresponding acids are very corrosive. Some of the problems with alternative Sn/Pb plating electrolytes are summarized below:

H_2SO_4, HCl	Precipitation of $PbSO_4$, $PbCl_2$
HNO_3	Cathodic decomposition of nitrate
$MeCO_2H$	Low conductivity
HBF_4, H_2SiF_6	Environmental problems H_2NSO_3H,
$H_2S_2O_6$	Hydrolysis problems, low conductivity

Complexation and hydrolysis; especially with respect to Pb(II)

The methanesulfonate ion forms less stable metal complexes than do the fluoroborate, fluorosilicate and associated fluoride ions.[22,25] The complexing nature of the fluoroborate, fluorosilicate and fluoride anions make it difficult to efficiently remove metal ions (*e.g.*, Pb^{2+}) from effluent streams. By far the most common method of dealing with metal containing aqueous effluent solutions is by caustic precipitation of metal oxide followed by filtration. The caustic precipitation of lead, for instance, is shown in eqn. (7) (X^- = any anion).

$$Pb^{2+} + 2\ X^- + 2\ NaOH \rightarrow PbO\ (s) + H_2O + 2\ NaX \qquad (7)$$

The insoluble lead oxide formed is removed from the aqueous effluent by filtration. The optimal conditions for caustic precipitation of metal ions vary depending on the metals present. For Pb(II), a pH of about 9 results in the maximum removal of lead *via* precipitation of the oxide. The amount of lead left dissolved in an aqueous effluent solution after caustic precipitation is strongly dependent upon the complexing nature of the anions present. A generic example of the competition between caustic precipitation of Pb(II) and anionic complexation of Pb(II) is shown in eqn. (8).

$$3\ Pb^{2+} + 6\ X^- + 4\ NaOH \rightarrow Na_4PbX_6 + 2\ H_2O + 2\ PbO(s) \qquad (8)$$

In eqn. (8), an octahedral distribution of ligands around Pb(II) is assumed. In practice, the actual structure of any lead complex formed will depend upon the nature of the anion X^- and the conditions present in the solution. Basically, the residual level of lead left in an effluent after a caustic precipitation operation is directly related to the complexing ability of the anions present in the effluent. The residual level of soluble Pb(II) left in solution after optimized caustic precipitation of lead from MSA(aq) based Sn/Pb plating solutions is less than 1 ppm, while the residual level of soluble Pb(II) left in solution after caustic precipitation of lead from HBF_4(aq) based solutions is typically more than 10 times as high.[26] Thus, caustic precipitation of $Pb(BF_4)_2$(aq) and/or $PbSiF_6$(aq) solutions leaves a significantly higher level of residual soluble lead than does caustic precipitation of $Pb(O_3SMe)_2$(aq) solutions. In addition, the residual lead level after caustic precipitation must be further reduced prior to discharge, and usually some sort of ion-exchange based technique is used for this purpose. As for the initial caustic precipitation process, the secondary removal of residual lead from treated HBF_4(aq) and H_2SiF_6(aq) solutions, as compared to treated MSA(aq) solutions, is also more difficult. In total, the lower toxicity and greater ease of waste treatment of MSA based solutions makes MSA the ‘green’ choice for commercial electrolytes, especially those containing lead.

Another problem with fluoroboric acid and fluorosilicic acid based electrochemical electrolytes is the tendency for these acids to be anodically hydrolyzed. Hydrolysis results in dissociation, and both processes are accelerated by the local acidification which inevitably occurs near the anode. Note that there are also hydroxide ion initiated hydrolysis reactions of fluoroboric acid and fluorosilicic acid, but such reactions are not important in acidic electrolytes. The dissociation of fluoroboric acid and fluorosilicic acid results in the production of the volatile species HF, BF_3 and SiF_4, and the hazards associated with these materials are well known (see Comparative Toxicity section of this paper). The simple dissociations of fluoroboric acid and fluorosilicic acid are shown in eqns. (9a) and (9b).

$$HBF_4 \rightarrow HF + BF_3(g) \qquad (9a)$$
$$H_2SiF_6 \rightarrow 2\ HF + SiF_4(g) \qquad (9b)$$

Fluoroboric acid is normally stabilized by the addition of an excess of boric acid (H_3BO_3), and fluorosilicic acid is normally stabilized by the addition of an excess of silicic acid (H_2SiO_3). These additives partially suppress the evolution of HF from fluoroboric and/or fluorosilicic acid based electrolytes, but the stabilizing effect is greatly compromised in the vicinity of the anode. Anodic acid generation creates local conditions which greatly accelerate HBF_4 and H_2SiF_6 decomposition. Such acidic anode conditions can be generated on both soluble anodes and insoluble anodes. By definition, soluble anodes are prepared from metals which will anodically dissolve into the electrolyte (*e.g.*, Sn/Pb electrodeposition processes normally employ soluble Sn/Pb anodes with a Sn/Pb composition which is similar to that present in the plating electrolyte). Insoluble anodes are prepared from materials which will not anodically dissolve into the electrolyte, and such anodes are designed to maximize the oxidation of a component in the electrolyte (*e.g.*, the oxidation of H_2O into O_2 and H^+, or the oxidation of Cl^- to Cl_2).

In addition to the dissociation caused by local anode acidification, there is also a catalytic acceleration of fluoroboric acid and fluorosilicic acid dissociation by many soluble anode slime layers. Soluble anodes which do not completely dissolve during electrolysis become covered with an insoluble residue which is commonly called a slime layer. Soluble anode slime layers are composed of residual poorly soluble impurities which were present in the original anode material. Soluble Sn/Pb anodes and crude lead bullion anodes, for instance, form slime layers. In the case of Sn/Pb electroplating, the formation of an anode slime layer is mostly an unavoidable inconvenience; while for lead electrorefining, the formation of a thick anode slime layer is an integral part of the basic process. In any event, both fluoroboric acid and fluorosilicic acid tend to dissociate within anode slime layers.[27] MSA, on the other hand, does not undergo anodic degradation as a result of local anode acidification and/or anode slime layer catalysis. Under the electrolysis conditions (current density, solution composition, *etc.*) normally employed for electroplating (*e.g.*, Sn/Pb electroplating) and electrorefining (*e.g.*, lead electrorefining), MSA is essentially completely stable (see electrowinning procedure 4, Experimental section).

Lead fluorosilicate, lead fluoroborate and lead methanesulfonate all possess good functional properties with respect to the electrochemistry of Pb(II) in aqueous solutions, and indeed these three electrolytes have been the standards for various electrochemical processes involving lead. In addition to functional properties, environmental and safety properties (known generically as ‘green’ properties) are also important, and since the early 1980s the superior ‘green’ character of MSA as compared to fluoroboric and fluorosilicic acid has become increasingly important.

The market for MSA in electrochemical processing

Methanesulfonic acid is a relatively new development in the world of electrochemical processing, having been made available commercially for the first time by Pennwalt Corporation in 1964.

In comparison, fluoroboric and fluorosilicic acid have been commercially available since the early 1900s. The late arrival of MSA was largely due to the relatively greater difficulty of preparing alkanesulfonic acids like MSA on a large scale, and MSA remained a technical curiosity until Pennwalt Corporation developed an industrial manufacturing process in 1964 (see references in the Industrial Production section above). Since the preparation of typical alkanesulfonic acids requires considerably greater effort than does the preparation of commodity acids (*e.g.*, H_2SO_4, HCl, H_2SiF_6), the price of alkanesulfonic acids is significantly higher than the price of commodity acids. The current price of some acids which allow for the convenient preparation of water soluble lead are shown in Table 4. The criterion of water soluble lead salts was used because electrochemical applications involving lead are the most significant for MSA.

Table 4 The current cost of some acids which yield soluble lead salts

Acid (commercial concentration)	Price quote ($\$ lb^{-1}$, absolute basis)	Source (date)
Acetic acid (99.7%), $MeCO_2H$	0.36	CMR[a] (1/22/99)
Fluoroboric acid (50%), HBF_4	1.05	CMR (1/22/99)
Fluorosilicic acid (318 g L^{-1}), H_2SiF_6	0.65	Cominco[b] (3/1/99)
Methanesulfonic acid (70%), $MeSO_3H$	2.20	Elf Atochem[c] (2/10/99)
Nitric acid (70%), HNO_3	0.10	CMR (1/22/99)

[a] *Chem. Mark. Rep.*, 1999, **255**, 28. [b] Quote, Cominco, Trail, BC, Canada (Consumer of Fluorosilicic Acid). [c] Quote, Elf Atochem NA, Philadelphia, PA, USA (Producer of MSA).

Conclusions

During the past twenty years, methanesulfonic acid ($MeSO_3H$) has largely replaced fluoroboric acid (HBF_4) as the electrolyte of choice for the electrodeposition of Sn/Pb solder on electronic devices. Certain other electrochemical processes involving lead, most notably the electrorefining of lead by the Bett's process, are currently carried out in fluorosilicic acid (H_2SiF_6) based electrolytes, but MSA based electrolytes are being actively investigated as environmentally superior alternatives to the currently used systems. Also, a number of commercial strip steel tin plating operations have recently converted to MSA based tin plating electrolytes.[28] There are also developing markets for MSA in Ag,[29] Ni,[30] Cu[31] and Zn[32] electroplating. These changes have been driven by the superior functional properties and environmental advantages of methanesulfonic acid (MSA).

The benefits of MSA(aq) include:

1. Excellent metal salt solubility
2. Excellent conductivity
3. Ease of effluent treatment
4. Stability
5. Low toxicity and biodegradability

With respect to electrochemical processes involving lead, MSA based process electrolytes are particularly advantageous in that they are less toxic and easier to waste treat than the existing alternatives. Into the foreseeable future, industrial electrochemical processes, especially those involving tin and lead, will likely continue to be converted to safe, functional, efficient and environmentally friendly MSA.

Experimental

Methanesulfonic acid (MSA) [75-75-2] and ethanesulfonic acid (ESA) [594-45-6] were obtained as 70% aqueous solutions from Elf Atochem NA. Hydrochloric acid and sulfuric acid were purchased from Aldrich Chemical Company. All chloride, sulfate, hydroxide and carbonate salts were purchased from Aldrich Chemical Company (Milwaukee, Wisconsin, USA).

Propanesulfonic acid (PSA) [226-114-2]

Prepared from propanesulfonyl chloride (PSC) [10147-36-1]. Crude PSC was obtained from Elf Atochem NA. The crude PSC was distilled (bp = 85 °C, 17 mm) to improve its purity (98% after distillation). The reaction was carried out by vigorously mixing H_2O (500 g) and PSC (1000 g) while slowly increasing the reaction temperature (*ca.* 1 °C min^{-1}) to *ca.* 110 °C. Care should be taken to insure that the reaction temperature is not increased too quickly, as the reaction can 'take-off'. If the reaction starts to overheat, then some control can be gained by slowing the stirring rate. While we had no trouble adding all the reactants together at once, one can for added control add the PSC to the reaction in small portions. After the initial heating, the hydrolysis was continued at 110 °C for 4 h, during which time evolved HCl was absorbed in a caustic trap. The crude 70% PSA(aq) which resulted was then heated with stirring to 100 °C under aspirator vacuum (*ca.*1 40 mmHg) for several hours to remove residual HCl. Nitrogen was bled (*ca.* 1 cm^3 s^{-1}) through the system to both assist in the removal of HCl(g) and to prevent darkening of the product. Occasional additions of doubly ionized (DI) H_2O were used to make up for volume lost during the HCl stripping process. After HCl removal was complete, the PSA(aq) was cooled slightly and *ca.* 4 mL of 30% H_2O_2(aq) per liter of 70% PSA(aq) was added to decolorize and deodorize the final product. The peroxide treated PSA(aq) was heated to 100 °C for several hours (under a nitrogen gas blanket) to guarantee complete destruction of residual peroxide (at room temperature, low levels of H_2O_2 can persist for months in 70% aqueous PSA). Typical PSA(aq) analysis was: clear color, no odor, no observable particles, assay = 70% w/w, density = 1.2 g cm^{-3}, molarity = 6.7 M (5.6 meq. PSA per g solution), sulfate level (by ion chromatography) = 70 ppm, chloride level (by IC) = 30–2000 ppm (depending on HCl stripping conditions), organic extractable impurities (CH_2Cl_2 extraction, by GC) = 50–2000 ppm (depending on H_2O_2 post-treatment conditions), residual PSC (CH_2Cl_2 extraction, by GC) = 0–1000 ppm (depending on hydrolysis conditions), residual peroxide (by titration) = 0–250 ppm (depending on H_2O_2 destruction conditions).

The preparative procedures for the alkanesulfonate salts are given below. Note that in most cases the salts were washed with solvents (*e.g.*, acetone, isopropyl alcohol, diethyl ether). The solvent volumes used (not specified below) were in all cases minimal. Generally a volume of acetone and/or isopropyl alcohol equal to the volume of the solid produced was employed, and a volume of ether equal to about 1/3 of the volume of solid produced was employed. All used wash solvent was disposed of in an appropriate manner. The initial solvent wash (acetone or isopropyl alcohol) was employed to remove excess sulfonic acid. This solvent wash could be avoided when time was available for careful aqueous recrystallization of the product. The second solvent wash (ether) was used to facilitate drying. The second solvent washing was not necessary when sufficient time was available to dry the product in a vacuum oven. Note that ether is very flammable, and the use of all solvents, especially ether, should only be undertaken by individuals with knowledge of the hazards involved. The solvent washing steps were employed as a convenient way to prepare small amounts of pure salts in a short period of time. Methods involving aqueous recrystallization and vacuum drying would certainly be more environmentally acceptable for the production of large amounts of material. In all cases, the identity and purity of the metal methanesulfonate product was established by % metal and % sulfur (methanesulfonate) analysis (AA spectroscopy and/or ICP/emission). In certain cases, IC analysis was used to corroborate the AA/ICP results. As the salts were often isolated as hydrates with non-stoichiometric amounts of associated water, the purity analysis was most conveniently reported in terms of the ratio of % metal to % sulfur (methanesulfonate). Note that this ratio is easily calculable by the following formula; (% metal / % sulfur) = [GMW(metal)]/[metal valence × 32.06(GMW of S)] (GMW = gram molecular weight).

Ammonium methanesulfonate [22515-76-0] 1

Equimolar amounts of MSA (1 mol of MSA as a 70% aqueous solution) and ammonia (1 mol of NH_3 as a 29% aqueous solution) were reacted together at room temperature. Water was removed from the reaction mixture *in vacuo* (4 mmHg), and the crystalline residue was washed with a small amount of isopropyl alcohol and ether. The solid product was reduced to a constant weight *in vacuo* (1 mmHg). Theoretical yield = 112 g, actual yield = 98 g (87%).

Lithium methanesulfonate [2550-62-1] 2

Lithium hydroxide monohydrate (42 g, 1 mol) was slowly added to 70% MSA (aq, 140 g, 1 mol) over 10 min with stirring. The homogeneous solution was reduced *in vacuo* (4 mmHg) to a solid residue, and the solid residue was washed with acetone and ether (to remove excess MSA). The solid product was reduced to a constant weight *in vacuo* (1 mmHg). Theoretical yield = 102 g, actual yield = 83 g (81%). For LiOMs; %Li/%S (theoretical) = 0.22, %Li/%S (actual) = 0.21.

Sodium methanesulfonate [2386-57-4] 3

Available from Aldrich Chemical Company. Reported purity of 98%.

Potassium methanesulfonate [2386-56-3] 4

Prepared with a method similar to that used for the preparation of the lithium salt of MSA except that isopropyl alcohol was used in place of acetone. Theoretical yield = 134 g, actual yield = 118 g (88%). For KOMs; %K/%S (theoretical) = 1.22, %K/%S (actual) = 1.20.

Magnesium methanesulfonate [62512-10-1] 5

Solid magnesium hydroxide (30 g, 0.51 mol) was slowly added to 70% MSA (aq, 142 g, 1.03 mol, 1% excess, heated to 80 °C, keep the solution temperature below 90 °C during addition). A small amount of DI H_2O (10 ml) was added to clarify the solution, and then the solution was allowed to cool to room temperature. $Mg(O_3SMe)_2$ precipitated from the solution upon cooling. The crystalline product was collected by vacuum filtration and washed with isopropyl alcohol and ether. The product was evaporated to constant weight *in vacuo* (1 mmHg). Theoretical yield = 214.5 g, actual yield = 123 g (57%). For $Mg(O_3SMe)_2·9H_2O$; %Mg/%S (theoretical) = 0.38, %Mg/%S (actual) = 0.37.

Calcium methanesulfonate [58131-47-8] 6

A 1 L beaker was charged with 70% MSA (aq, 310 g, 2.26 mol, 3% excess, heated to 90 °C). Finely powdered $CaCO_3$ (110 g, 1.10 mol) was added with stirring over *ca.* 1 h. Small additions of DI H_2O were used to wash solid $CaCO_3$ down the sides of the beaker. When the addition was complete, the temperature of the solution was brought to 100 °C and DI H_2O was added until the solution became clear. The clear solution was decanted away from solid particulates and then evaporated *in vacuo* (4 mmHg) to give a crystalline residue. The crystalline residue was washed with isopropyl alcohol and ether. The solid product was evaporated to constant weight *in vacuo* (1 mmHg). Theoretical yield = 253.1 g, actual yield = 94.1 g, (37%). For $Ca(O_3SMe)_2$; %Ca/%S (theoretical) = 0.63, %Ca/%S (actual) = 0.62.

Strontium methanesulfonate 7

A 500 mL beaker was charged with 70% MSA (aq, 75 g, 0.547 mol, 40% excess), powdered strontium carbonate (25 g, 0.160 mol), and DI H_2O (20 mL). The mixture was stirred overnight and then filtered through a 1 μm glass microfiber pad. The clear filtrate was evaporated *in vacuo* (4 mmHg) to a crystalline residue. The crystalline residue was washed with isopropyl alcohol and ether. The solid product was evaporated to constant weight *in vacuo* (1 mmHg). Theoretical yield = 44.4 g, actual yield = 42.1 g (95%).

Barium methanesulfonate [26755-96-4] 8

A 1 L beaker was charged with 70% MSA (aq, 274 g, 2 mol) and powdered barium carbonate (197 g, 1 mol). The mixture was stirred and heated (80 °C) while an additional portion of 70% MSA (aq, 100 g, 36% excess) was slowly added. After 1 h, enough DI H_2O was added to produce a homogeneous solution at 80 °C. A 50 ml dose of isopropyl alcohol was then added, and the still clear solution was allowed to cool to room temperature. The crystalline precipitate was collected by vacuum filtration and washed with isopropyl alcohol and ether. The solid product was brought to constant weight *in vacuo* (1 mmHg). Theoretical yield = 327.3 g, actual yield = 235 g (72%). For $Ba(O_3SMe)_2$; %Ba/%S (theoretical) = 2.14, %Ba/%S (actual) = 2.16.

Mn(II) [88576-27-6] 9, Co(II) [50910-89-9, dihydrate] 10, Ni(II) [55136-38-4] 11 and Cu(II) [54253-62-2] 12 salts of MSA

All prepared from the corresponding carbonates using methods similar to those described above. In some cases, filtration of an aqueous solution of the product was necessary [*e.g.*, to remove MnO_2 from $Mn(O_3SMe)_2$]. For $Mn(O_3SMe)_2·2H_2O$; %Mn/%S (theoretical) = 0.86, %Mn/%S (actual) = 0.87. For $Co(O_3SMe)_2·4H_2O$; %Co/%S (theoretical) = 0.92, %Co/%S (actual) = 0.92. For $Cu(O_3SMe)_2·4H_2O$; %Cu/%S (theoretical) = 0.99, %Cu/%S (actual) = 0.98.

The preparation of silver methanesulfonate was accomplished by each of the general methods discussed above. All four procedures are given below for comparative purposes.

Silver(I) methanesulfonate [2386-52-9] 13

From Ag_2O

To 500 g of 70% MSA (aq, 3.64 mol) in a 1 gallon beaker, 402 g of silver oxide (3.47 mol of Ag^+) was slowly added over 30 min so as to form a uniform suspension. The temperature of the reaction mixture rose to *ca.* 60 °C during the addition, and this temperature was maintained with heating for an additional 4 h. The reaction mixture was filtered through a thick 1 μm glass microfiber pad, and the filtrate was stripped *in vacuo* (4 mmHg) to a solid residue. The solid residue was washed with isopropyl alcohol and ether. Finally the crystalline product was reduced to constant weight *in vacuo* (1 mmHg). Theoretical yield = 704 g, actual yield = 450 g (64%). For Ag(OMs); %Ag/%S (theoretical) = 3.36, %Ag/%S (actual) = 3.37.

From ligand metathesis between MSA and $AgNO_3$

Note that the following procedure is given for informational purposes only. This method would not normally be recommended for the preparation of AgO_3SMe. Nitrate salts can be dangerous, and while we experienced no problem with this preparation it is still recommended that the entire procedure be conducted behind an explosion shield. A 100 mL round bottomed flask was charged with $AgNO_3$ (17.25 g, 101 mmol) and 70% MSA (14.5 g, 106 mmol). The flask was fitted with a condenser and 100 mL receiving flask. The receiving flask was ice cooled. The reaction mixture was stirred and put under aspirator vacuum (14 mmHg). The stirred reaction solution was gently heated to 90 °C and then left at this temperature for several hours during which time nitric acid distilled into the cooled receiving flask. After most of the nitric acid distilled over, the flask, still under vacuum, was heated further to an ultimate temperature of 170 °C. The flask was then cooled and the solid AgO_3SMe product removed. The crude product was washed with some acetone and ether to yield a final product with <100 ppm of residual nitrate. The yield was close to 100%. Overall purity as described above for AgO_3SMe produced from Ag_2O.

From chemical oxidation of Ag metal[33]

Hydrogen peroxide (93 mmol, 2 × excess) was added to a stirred mixture of silver metal (10 g, 93 mmol) in 20 mL of 70% MSA (aq) at such a rate that the temperature during the addition was kept below 45 °C. Following peroxide addition, the solution was stirred and the solution temperature maintained at 35 °C. A drop of the solution was tested at regular intervals for unreacted oxidant (iodide/starch color test). After all the oxidant had been consumed (reaction time strongly dependent on the surface area of the silver used), an additional portion of hydrogen peroxide (93 mmol) was added as before. Again, the solution was stirred and the solution temperature maintained at 35 °C. Following consumption of the second portion of oxidant, the reaction mixture was vacuum filtered through a 1 μm glass filter pad. The time-averaged rate of the reaction, under the conditions listed above, was *ca.* 1 mg Ag dissolution per hour per cm^2 of silver surface area. The higher the specific surface area ($cm^2\ g^{-1}$) of the metallic silver employed, the greater the absolute rate of the oxidative dissolution. With very fine silver powders (350 mesh and finer), the reaction evolved enough heat to create a need for vigorous cooling during the initial peroxide addition and throughout the reaction. The reaction time for fine silver powders was normally several hours. Note that reaction temperatures above 50 °C led to excessive decomposition of the hydrogen peroxide. With silver powders of intermediate fineness (*ca.* 100 mesh), the reaction took about 18 h. With silver chunks cut from a slab, the reaction was too slow to be be considered convenient. The consumption of the silver was between 10 and 95% depending on the fineness of the silver and the exact conditions employed. The reaction yield was close to 100% relative to the silver consumed. The reaction yield was between 10 and 45% relative to the hydrogen peroxide consumed, depending on the exact conditions employed. Purity as described above for AgO_3SMe produced from Ag_2O.

From anodic oxidation of Ag metal

An anion-exchange membrane (50 cm^2, ESC-7001, available from the Electrosynthesis Company, Lancaster, NY, USA) divided electrochemical tank cell (homemade) with a 1 L anolyte and catholyte compartment was fitted with a 60 cm^2 (one side) Ag anode and a 60 cm^2 (one side) Ni cathode (inter-electrode distance = 6 cm). The anolyte chamber was charged with 1 kg of 2% MSA(aq) wt/wt, and the catholyte chamber was charged with 1 L of 25% MSA(aq) wt/v. The anode process was oxidative silver dissolution. The cathode process was hydrogen formation. The membrane process involved passage of methanesulfonate from the catholyte into the anolyte. A current of 4 A (*ca.* 5 V) was passed for 6 h, and then the current was dropped to 1 A (*ca.*. 3 V) for 14 h (overnight). Note that the temperature of the solution increased over 2 h to a final steady 33 °C. The conductivity of the cell decreased throughout the experiment. The current was stopped, and the anolyte was removed and evaporated to yield a solid. The solid was washed with a small amount of acetone and ether. The final weight of AgO_3SMe was 218 g (76% current efficiency). Purity as described above for AgO_3SMe produced from Ag_2O.

Zn(II) [33684-80-9] 14, Cd(II) [74440-47-4] 15 and Sn(II) [53408-94-9] 16 salts of MSA

All prepared from the corresponding oxides using methods similar to those described above. Care should be taken in the preparation of tin(II) salts to exclude oxygen, as oxidation of Sn(II) to Sn(IV) can be troublesome. For $Zn(O_3SMe)_2{\cdot}2H_2O$; %Zn/%S (theoretical) = 1.02, %Zn/%S (actual) = 1.03. For $Sn(O_3SMe)_2{\cdot}2H_2O$; %Sn/%S (theoretical) = 1.84, %Sn/%S (actual) = 1.84.

Mercury(II) methanesulfonate [54253-64-4] 17

It should be noted that mercury compounds are highly toxic and proper protective equipment and procedures must be used at all times. The preparation of small amounts of this salt by the reaction of MSA(aq) with HgO was inconvenient. Instead, the target compound was obtained by heating an equinormal mixture of $Hg(NO_3)_2$ and 70% MSA(aq) under vacuum (30 mmHg, Teflon lined vacuum pump, caustic trap on the outlet of the pump). The temperature of the stirred mixture was slowly raised to *ca.* 100 °C (T_{max} = 110 °C), and the heating was continued for several hours until all the nitrate was removed as nitric acid. Though no tendency for energetic decomposition was noted, it is known that certain nitrate compounds can be unstable. As a precaution, the reaction apparatus was placed behind an explosion shield. The residual nitrate level in the final product was <300 ppm. Note that this procedure was employed with care and only used for the preparation of small amounts (5 g or less) of mercury(II) methanesulfonate. For $Hg(O_3SMe)_2$; %Hg/%S (theoretical) = 3.13, %Hg/%S (actual) = 3.12.

Lead(II) methanesulfonate [17570-76-2] 18

Prepared from $PbCO_3$ using a method similar to those described above. For $Pb(O_3SMe)_2$; %Pb/%S (theoretical) = 3.24, %Pb/%S (actual) = 3.21.

The following salts were used in the undivided cell electrowinning experiments.

Palladium(II) methanesulfonate [74109-53-8] 19

In a 50 mL beaker, 350 mesh palladium powder (1.06 g, 10 mmol), 70% MSA(aq) (2.72 g, 2 mL, 20 mmol) and 1.4 g of conc. HNO_3 (aq) (1 mL, 16 mmol) were mixed. The reaction was initiated by addition of one drop of conc. HCl(aq). The solid suspension rapidly turned dark brown, and the reaction was complete within 30 min. Further work-up could result in a solid product, but we opted to use a diluted solution, [Pd] = 5 g L^{-1}, of the crude reaction product directly in the next step (see electrowinning section of the Experimental section).

Copper(II) propanesulfonate [25321-66-8, tetrahydrate] 20

A 1 L beaker was charged with 200 g of 71% aqueous propanesulfonic acid (1.14 mol). To this was slowly added 63 g of basic copper carbonate (0.285 mol, 1.14 equiv) suspended in 100 mL of DI H_2O (final solution pH = 1.0). The solution was stirred at room temp. for 2 h and then filtered through a 1 µm glass microfiber pad. The filtrate was stripped *in vacuo* (4 mmHg) to a solid residue, and the residue washed with acetone and ether. The solid product was taken to constant weight *in vacuo* (1 mmHg). Theoretical yield = 176 g, actual yield = 162 g (92%).

Tin(II) ethanesulfonate [72437-74-2] 21

A 2 L flask was charged with 600 g of 70% aqueous ESA (3.81 mol, 3% excess) and then sparged with nitrogen gas. A 250 g portion of SnO (1.85 mol, 3.7 equiv.) was added with stirring and gentle N_2(g) sparging over 60 min. The reaction temperature increased from 23 to 30 °C during the addition. After stirring for 4 h under N_2(g), the solution was filtered through a 1 µm glass microfiber pad. The filtrate was stripped to dryness *in vacuo* (3 mmHg), and the solid residue was washed with acetone (isopropyl alcohol dissolves too much product) and ether. The product was taken to constant weight *in vacuo* (1 mmHg). Theoretical yield = 626 g, actual yield = 200 g (32%). The yield was low owing to losses in the rinse. Further product could be obtained by stripping the rinse solvents. For $Sn(O_3SEt)_2$; %Sn/%S (theoretical) = 1.85, %Pb/%S (actual) = 1.83.

Nickel(II) propanesulfonate 22

A 2 L beaker was charged with 303 g of aqueous 70% PSA (1.70 mol) and heated to 50 °C. To this solution was slowly added 100 g of nickel carbonate hydroxide tetrahydrate (0.17 mol, 0.85 mol of Ni^{2+}, 1.70 equiv.) slurried with 100 ml of DI H_2O. After 4 h at 50 °C, the solution was cooled and filtered through a 1 µm glass microfiber pad. The filtrate was stripped *in vacuo* (4 mmHg) to a solid residue, and the solid residue was washed with acetone and ether. The solid product was taken to constant weight *in vacuo* (1 mmHg). Theoretical yield = 518 g, actual yield = 330 g (64%).

Cobalt(II) ethanesulfonate [50910-90-2, dihydrate] 23

A 1 L beaker was charged with 172 g of aqueous 70% ESA (1.09 mol), and to this was added 50.6 g of $Co(OH)_2$ (0.54 mol, 1.08 equiv.). The temperature rose from room temperature to 50 °C during the addition. The suspension was stirred overnight at room temperature and then filtered through a 1 µm glass microfiber pad. The filtrate was reduced *in vacuo* (3 mmHg) to a solid residue. The solid residue was washed with isopropyl alcohol and ether. The purified product was reduced to constant weight *in vacuo* (1 mmHg). Theoretical yield = 150 g, actual yield = 147 g (98%). For $Co(O_3SEt)_2$; %Co/%S (theoretical) = 0.92, %Co/%S (actual) = 0.92.

Cadmium(II) propanesulfonate 24

A 1 L beaker was charged with 210 g of 71% aqueous PSA (1.20 mol). To this was slowly added 100 g of $CdCO_3$ (0.58 mol, 1.16 equiv.) slurried with 100 ml of DI H_2O. After 2 h, the solution was filtered through a 1 µm glass microfiber pad. The filtrate was stripped *in vacuo* (4 mmHg) to a solid residue. The solid residue was washed with acetone and ether. The solid product was taken to constant weight *in vacuo* (1 mmHg). Theoretical yield = 208 g, actual yield = 104 g (92% yield).

Iron(II) methanesulfonate [56525-23-6] 25

A 1 gallon beaker was charged with 1.5 kg of 70% aqueous MSA (10.9 mol). To the well stirred solution was added 250 g of iron powder (4.5 mol, Aldrich, 10 µm 99.9%) in 8 g portions over 6 h (ensure adequate ventilation to remove the hydrogen gas formed). The solution was stirred at room temperature overnight and then filtered through a 1 µm glass microfiber pad. The final product was an aqueous solution with [Fe] = 67.2 g l^{-1} and free acidity = 0.50 M.

Zinc(II) propanesulfonate 26

A 2 L beaker was charged with 450 g of 70% aqueous PSA (2.54 mol). To this was slowly added 100 g of ZnO (1.22 mol, 2.44 equiv.) slurried with 100 ml of DI H_2O. After 6 h, the solution was filtered through a 1 µm glass microfiber pad. The filtrate was stripped *in vacuo* (4 mmHg) to a solid residue. The solid residue was washed with acetone and ether. The solid product was taken to constant weight *in vacuo* (1 mmHg). Theoretical yield = 380 g, actual yield = 360 g (95%).

Zinc(II) ethanesulfonate [154780-19-5] 27

A 2 L beaker was charged with 550 g of 70% aqueous ESA (3.5 mol, 2% excess). The ESA(aq) was heated to 80 °C and 140 g of ZnO (1.72 mol, 3.44 equiv.) was added over 30 min. The hot solution was allowed to partially cool before being reduced *in vacuo* (3 mmHg) to a solid residue. The product was washed with isopropyl alcohol and ether. The solid product was reduced to constant weight *in vacuo* (1 mmHg). Theoretical yield = 487 g, actual yield = 450 g (92%). For $Zn(O_3SEt)_2$; %Zn/%S (theoretical) = 1.02, %Zn/%S (actual) = 1.04.

Solubility measurements

The saturation aqueous solubility values were determined by measuring the metal content of saturated aqueous solutions using an ICP-emission technique. The experimental method involved cleaning a Kimble glass vial with 1 M HCl(aq) and DI water followed by the transfer of 2–4 g of sample into the clean glass vial and the addition of 2 mL of DI water along with a clean magnetic stir bar. The solution was stirred for 4 h at room temperature and then placed in a temperature controlled oven (22 ± 1 °C) for at least 48 h. During this equilibration period, particulate solids settled out. The saturated solution was removed from the controlled temperature chamber, and, for verification, the solution temperature was checked. The density of the saturated solution was determined by weighing an accurately measured volume of saturated solution. The density determination was repeated at least three times to ensure precision. Next, 0.2 ml of saturated solution was transferred into a volumetric flask and diluted to an appropriate volume. The percentage metal in the original saturated solution was determined *via* the use of a calibration curve developed with accurate standards. The analysis technique used was ICP-AES (inductively coupled plasma-atomic emission spectroscopy), except for the potassium and mercury salts which were analyzed by AA (atomic absorption spectroscopy). The analyses were repeated at least twice to insure precision. The data were compiled, and our results were compared to literature data, where such data were available (*e.g.*, for the sulfate and chloride salts), to ensure that there was no more than 5% relative error.

Conductivity measurements

Standard aqueous acid solutions were made up by adding an appropriate amount of acid to DI water. The concentrations of the various acid solutions were checked by pH titration. Conductivity values were determined using an Orion model 142 conductivity meter.

Electrowinning procedures

The acids and salts were obtained or prepared as described above. The divided cell electrowinning apparatus was designed and produced at Elf Atochem NA. The material presented below is essentially identical to experimental details included in a US patent application (08/798985) and in a presentation delivered to the *12th Annual International Forum on Electrolysis in the Chemical Industry*.[34]

Procedure 1; electrowinning of various metals from an undivided cell

A series of electrowinning experiments were performed in an undivided electrochemical cell charged with 250 ml of an appropriate aqueous solution of a metal alkanesulfonate salt. The cell was fitted with a stainless steel cathode (50 cm^2) and an IrO_2 (30 cm^2) coated titanium inert anode. The average interelectrode spacing was 2 in. A constant current of 3 A (cathode current density = 60 mA cm^{-2}, anode current density = 100 mA cm^{-2}) was passed through the cell until most of the metal was removed and/or a steady-state level of metal concentration was obtained. The solution temperature was not maintained at room temperature, and resistive heating normally raised the temperature of the solution from room temperature to 35 °C during the first hour of the electrolysis. The electrolysis temperature was allowed to stabilize at 35 °C for the remainder of the experiment. The volume of the solution was maintained constant throughout the electrolysis by occasional additions of distilled water. Following the passage of an appropriate amount of charge (calculated as current × time), the solutions were filtered and analyzed for metal and acid content. Representative data are tabulated in Table 5.

Procedure 2; electrowinning of iron from a divided cell

A divided cell electrowinning apparatus (see Fig. 1) was fitted with a stainless steel cathode (55.6 cm^2), an iridium oxide coated titanium mesh anode (33.3 cm^2) and an ESC 7001 anion exchange membrane (111.1 cm^2). The catholyte chamber was charged with 1 L of a 0.47 molar aqueous solution of iron(II)/iron(III) methanesulfonate. The anode chamber was charged with 1 L of 0.1% aqueous solution of methanesulfonic acid (*ca.* 0.01 M). A current of 3 A, at *ca.* 14 V, was passed for 24 h (2.7 Faradays of charge, cathode current density = 54 mA cm^{-2}, anode current density = 90 mA cm^{-2}, membrane current density = 27 mA cm^2). The compositions of the catholyte and analyte before/after electrolysis are shown in Table 6.

Procedure 3; electrowinning of nickel and acid transport in a divided cell

A divided cell electrowinning apparatus as described in procedure 2 was used for this experiment. The catholyte chamber was charged with 1 L of a spent electroless nickel bath (5 g L^{-1} Ni^{2+}, 40 mL L^{-1} lactic acid, 30 g L^{-1} hypophosphite) in which the pH had been raised from 4.8 to 8.5 with ammonia (color change from green to blue). The anolyte chamber was charged with 1 L of a 1% aqueous solution of methanesulfonic acid (*ca.* 0.1 M). A current of 1 A, at *ca.* 10 V, was passed for 32 h (1.2 Faradays of charge, cathode current density = 18 mA cm^{-2}, anode current density = 30 mA cm^{-2}, membrane current density = 9 mA cm^{-2}). The compositions of the catholyte and anolyte before and after electrolysis are shown in Table 7.

Procedure 4; electrolytic stability of methanesulfonic acid

The robustness of aqueous alkanesulfonic acid electrolytes was assessed by subjecting 10% aqueous solutions of MSA (*ca.* 1 M) to 24 h of electrolysis (production of hydrogen on the cathode, production of oxygen on the anode) at various current densities in an undivided cell. The cathode was a piece of polished silver. The anode was an IrO_2 coated titanium mesh. The increase in the sulfate concentration of MSA solutions following 24 h of electrolysis at various current densities is tabulated in Table 8.

The low levels of sulfate formation, even after 24 h of electrolysis at useful electrowinning current densities, illustrate the robustness of aqueous methanesulfonic acid (MSA) based electrolytes. The small amount of sulfate which did form was produced *via* a poorly characterized anodic oxidation of both MSA and certain low level impurities (*e.g.*, dimethyl sulfone) commonly present in MSA.

Addendum; metal alkanesulfonate preparations

The metal methanesulfonate salts used in this study were produced by employing one of the four general methods discussed below. Note that detailed experimental procedures are given in the Experimental section.

Generically, all simple metal salts are produced by metathesis reactions. Such metatheses can either be between two metal salts (one containing the anion and the other containing the cation sought) or they can be between the acid form of the desired anion and a metal salt containing the desired metal cation. A general depiction of the two processes are represented below in eqns. (10a) and (10b).

$$ML_n + M'X_n \rightarrow M'L_n + MX_n \qquad (10a)$$
$$ML_n + n\,HX \rightarrow MX_n + n\,HL \qquad (10b)$$

For a salt preparation to be successful, either the equilibrium must favor the product or the equilibrium must somehow be shifted toward the product. In addition, for the recovery of a pure salt, the by-product (HL or ML) must be readily separable from the product (MX_n). The equilibria can be shifted toward the product by, for instance, the application of sufficient voltage (electrochemical process), or by the constant removal of the ML_n or HL by-product (chemical process). By-product removal can be accomplished by simple *in vacuo* distillation (*e.g.*, with a volatile acid by-product) or by solubility driven precipitation (*e.g.*, with AgCl or $CaSO_4$ by-product). Even in cases where a zero-valent metal is chemically oxidized to a desired salt, reaction (10b) is applicable, as an intermediate reactant salt will be produced *in situ* by the action of the oxidizing agent on the metal.

Perhaps the most straight-forward method for producing a simple metal salt involves the reaction of equinormal amounts of a basic metal salt with the acid form of the anion of interest (acid plus a base yields a salt). Typical basic metal salts include carbonates, hydroxides and oxides. In this case, the equilibrium lies naturally to the right, and the product is readily isolated by the removal of by-product water *in vacuo*. In our case, we reacted the

Table 5 Experimental data from electrowinning experiments in an undivided cell with metal alkanesulfonates

Metal[a]	[Metal] (initial)[b]/g L^{-1} (M)	[Metal] (final)[c]/g L^{-1} (M)	[Acid] (initial)[d]/ mol kg^{-1}	[Acid] (final)[e]/ mol kg^{-1}	Completion M/A[f] (%)	Current efficiency[g] (%)
Palladium (MS)[h] **19**	4.5 (0.04)	0 (0)	0.03	0.15	100/150	57
Silver (MS) **13**	109 (1.01)	3 (0.03)	0.02	0.97	97/97	53
Copper (PS) **20**	63 (0.99)	0.2 (0.003)	0.01	2.01	99 /106	79
Tin (ES) **21**	59 (0.50)	0.4 (0.003)	0.05	1.01	99/96	85
Lead (MS) **18**	184 (0.89)	0.4 (0.002)	0.01	2.01	100/112	130[i]
Nickel (PS) **22**	51 (0.87)	36 (0.61)	0.02	0.55	29/102	17
Cobalt (ES) **23**	55 (0.93)	40 (0.68)	0.01	0.68	27/134	14
Cadmium (PS) **24**	66 (0.59)	0.1 (0.001)	0.04	1.61	100/133	46
Iron (MS) **25**	54 (0.97)	46 (0.82)	0.02	1.01	15/330	81
Iron/tin[j] (MS)	26 (0.46)	26 (0.46)	0.22	0.36[k]	0/UD[l]	UD[l]
Zinc (PS) **26**	56 (0.86)	18 (0.27)	0.03	1.21	68/100	23
Zinc (ES) **27**[m]	66 (1.01)	5 (0.08)	0.01	1.54	92/82	52

[a] Metals were dissolved in DI H_2O as Pd(II), Ag(I), Cu(II), Sn(II), Pb(II), Ni(II), Co(II), Cd(II), Fe(II)/(III), Zn(II). [b] The initial concentration of the metal before electrowinning expressed as g metal per liter of solution with molarity in parentheses; by ICP/emission analysis. [c] The final concentration of the metal following electrowinning expressed as g metal per liter of solution with molarity in parentheses; by ICP/emission analysis. [d] The initial concentration of strong acid before electrowinning expressed as mol H^+ per kg solution; by pH titration. [e] The final concentration of strong acid after electrowinning expressed as mol H^+ per kg solution; by pH titration. [f] The percentage completion of the process (M/A) based on: M: the amount of metal removed from solution relative to the total amount of metal originally present. A: the amount of acid present in the final solution relative to the total amount possible for the amount of metal removed by electrodeposition. Values of A which are >100% are the result of measurement uncertainties, unknown variables and/or the formation of soluble/suspended high valent metal oxide compounds. High valent metal oxide compounds yield excess acid upon formation, but the metal compounds also continue to remain in solution. The formation of high valent metal oxide compounds results in net acid production without the metal being removed from solution. Values of A which are <100% result from measurement uncertainty. [g] The percentage current efficiency of the process based on the amount of metal removed. The current efficiency was calculated as mn/q (m = mol metal removed, n = metal valence, q = mol equiv. of charge passed). The total charge passed (TCP), in coulombs, can be calculated as [(mol metal removed) × (metal valence) × (1/current efficiency) × 96,487]; the total electrolysis time, in s, can be calculated as TCP/(3), a current of 3 A was used. [h] MS = methanesulfonate, ES = ethanesulfonate, PS = propanesulfonate. [i] A current efficiency of >100% was obtained because lead was being removed at both electrodes. [j] Sample obtained from an operational Fe removal system (analysis = 0.46 M Fe, 0.08 M Sn, 0.22 M MS). [k] This acid was generated by the efficient electrowinning of the small amount of tin which was present in the solution. [l] UD = undefined; acid recovery values and current efficiency relative to the iron concentration are undefined. [m] This experiment employed a special high surface area carbon cathode for the final stages of the electrowinning.

Table 6 The electrowinning of iron from a divided electrowinning cell

Chamber[a]	[Iron] (initial)[b]/g L^{-1} (M)	[Iron] (final)[c]/g L^{-1} (M)	[Acid] (initial)[d]/m	[Acid] (final)[e]/m	Completion[f] (%)	Current efficiency (%)
Catholyte	26.2 (0.47)	0.9 (0.02)	0.02	0.02	96	33[g]
Anolyte	26.0 (0)		0.01	0.88	98	32[h]

[a] The chamber of the divided electrowinning cell. [b] The initial concentration of the metal before electrowinning expressed as g metal per liter of solution with molarity in parentheses; determination by ICP/emission analysis. [c] The final concentration of the metal following electrowinning expressed as g metal per liter of solution with molarity in parentheses; determination by ICP/emission analysis. [d] Initial concentration of strong acid before electrowinning expressed as mol protons per kg solution; by pH titration. [e] Final concentration of strong acid after electrowinning expressed as mol protons per kg solution; by pH titration. [f] Catholyte: the percentage completion based on the amount of metal removed. Anolyte: the percentage completion based on the amount of acid produced relative to the total amount of iron removed. [g] Cathode: the percentage current efficiency based on mol of metal removed per mol of charge passed. The current efficiency was calculated as mn/q (m = mol metal removed, n = metal valence, q = mol equivalents charge passed). [h] Anode: the percentage current efficiency (oxygen evolution with regeneration of acid) was close to 100%; the observed inefficiency (apparent inefficiency) was due to the leakage of protons across the membrane. The percentage current efficiency was calculated as H/q (H = mol of recoverable acid generated, q = mol equivalents of charge passed).

desired alkanesulfonic acid with a commercially available basic metal salt. The preparations of sodium (**3**), lead (**18**) and silver (**13**) methanesulfonate are shown in eqns. (11)–(13).

$$NaOH + MeSO_3H \rightarrow NaO_3SMe + H_2O \tag{11}$$

$$PbCO_3 + 2\ MeSO_3H \rightarrow Pb(O_3SMe)_2 + H_2O + CO_2 \tag{12}$$

$$Ag_2O + 2\ MeSO_3H \rightarrow 2\ AgO_3SMe + H_2O \tag{13}$$

A less common method of salt manufacture involves ligand metathesis between an acid and an acidic salt. In this case, the equilibrium does not lie strongly to the right, and the reaction must be driven forward by the continuous removal of at least one reaction product. In our case, we mixed metal nitrates with alkanesulfonic acids, and we drove the reaction to completion by the continuous removal of nitric acid *via* vacuum distillation. This method was used by us in the preparation of silver (**13**) and

Table 7 The electrowinning of nickel in a divided electrowinning cell

Chamber	[Ni] (initial)/g L^{-1} (M)	[Ni] (final)/g L^{-1} (M)	[Acid] (initial)/ mmol g^{-1}	[Acid] (final)/ mmol g^{-1}
Catholyte	5 (0.08)	0	1.38	0
Anolyte	0	0	0.13	1.67[a]

[a] Acid concentrations in mmol protons per g solution. The 1.67 m acid in the anolyte at the end of the electrowinning experiment was composed of 9% acetic acid, 65% methanesulfonic acid and 26% lactic acid.

Table 8 The formation of sulfate from methanesulfonate under electrolysis conditions similar to those useful for electrowinning

Current density/mA cm^{-2}	Sulfate concentration (ppm)
Cathode = 32 mA cm^{-2}, anode = 20 mA cm^{-2}	12
Cathode = 64 mA cm^{-2}, anode = 40 mA cm^{-2}	12
Cathode = 96 mA cm^{-2}, anode = 60 mA cm^{-2}	14

mercury(II) (**17**) methanesulfonate, as shown in eqns. (14) and (15). It is interesting that the mercury(II) salts of methanesulfonic, ethanesulfonic and propanesulfonic acids were unusually unstable. In all three cases, we had trouble making these mercury(II) salts by simple acidification of mercuric oxide. The nitrate metathesis reaction provided us with a convenient method for making small amounts of these mercury(II) alkanesulfonate salts.

$$AgNO_3 + MeSO_3H \longrightarrow AgO_3Me + HNO_3\ (g)\uparrow \qquad (14)$$

$$Hg(NO_3)_2 + 2\ MeSO_3H \longrightarrow Hg(O_3SMe)_2 + HNO_3\ (g)\uparrow \qquad (15)$$

Another common method for the preparation of salts involves chemical or anodic oxidation of the metal of interest in an electrolyte containing the acid form of the desired anion. For chemical oxidation, this type of reaction can be thought of as *in situ* formation of a nascent metal oxide followed by acidification. Methods of this type generally avoid the problems associated with the sluggish reaction of passive metal oxides. Many metal oxides dehydrate and become somewhat passivated on standing (*e.g.*, precious metal oxides), and it is sometimes more convenient to react such oxides immediately as they are formed.

For anodic oxidation of a metal in an acid medium, the process can be viewed most simply as the direct introduction of the metal cation into the solution. Anodic (electrochemical) oxidation methods for the production of a metal salt require a method for preventing the metal cation of the salt from redepositing on the cathode. In general, divided electrochemical cells are employed for this purpose. The cells can be divided by simple micropore frits or, more desirably, by anion-exchange membranes. We developed chemical oxidations for the production of silver (**13**) and palladium (**19**) methanesulfonate, as shown in eqns. (16) and (17). We also developed an anodic oxidation for the production of silver methanesulfonate **13**, as shown in eqn. (18).

$$2\ Ag + H_2O_2 + 2\ MeSO_3H \longrightarrow 2\ AgO_3SMe + 2\ H_2O \qquad (16)$$

$$2\ Pd + 2\ HNO_3 + 4\ MeSO_3H \longrightarrow 2\ Pd(O_3SMe)_2 + 2\ NO + 12\ O_2 + 3\ H_2O \qquad (17)$$

$$Ag \longrightarrow Ag^+\ (anode) + e^- \quad MeSO_3H + e^- \longrightarrow 12\ H_2\ (g) + MeSO_3^-\ (cathode) \qquad (18)$$

It should be noted that silver methanesulfonate is a useful intermediate for the preparation of other metal methanesulfonate salts *via* AgCl precipitation driven reactions with appropriate metal chlorides. The basic reaction is shown below, for the preparation of tin(II) methanesulfonate, in eqn. (19).[35] The preparation of tin(II) methanesulfonate is hindered by the tendency for Sn(II) to oxidize to Sn(IV), and the use of AgO_3SMe is sometimes most convenient for laboratory scale preparations.

$$SnCl_2 + 2\ AgO_3SMe \longrightarrow Sn(O_3SMe)_2 + AgCl(s) \qquad (19)$$

A conceptually simple method for the production of metal salts involves simple acidic leaching of the desired metal. This reaction can be viewed as simple oxidation of the metal by protons. As such, this is the only method which does not formally involve any sort of cation/anion metathesis reaction, and this type of process, when possible, is the most simple. Such processes are commonly used in the recycle loops of zinc electroplating lines which employ inert anodes. The inert anodes for this application are designed to convert water into oxygen and acid. Inert, or insoluble, anodes are to be contrasted with soluble anodes which directly replace by oxidative dissolution the metal cation being electroplated out of the solution. Inert anodes are used despite the inconvenience they introduce, because they allow for a very exact inter-electrode spacing to be maintained. The use of oxygen generating inert anodes in a zinc electroplating system results in a steady increase in the acidity of and a decrease in the metal content of the electroplating solution. To balance the acidification caused by the use of such inert anodes in a zinc plating process, a portion of the operating plating solution is continually passed over zinc granules. The zinc granules react with the excess acid to yield a replenishing zinc salt. It is worth noting that care must be taken to insure that the hydrogen gas formed by this process is properly vented. In our case, we used acidic leaching for the production of iron(II) methanesulfonate **25** as shown in eqn. (20).

$$Fe + 2\ MeSO_3H \longrightarrow Fe(O_3SMe)_2 + 12\ H_2 \qquad (20)$$

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