# DEVELOPMENT OF REDOX FLOW BATTERIES. A HISTORICAL BIBLIOGRAPHY

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#### Summary

Redox-flow battery systems have been investigated for sixteen years. Initially developed in the U.S.A., such batteries have since interested many researchers worldwide. It seems that development is not yet exhausted and, in recent years, many industries (practically all in Japan) have made great efforts to produce practical cells.

In this paper, following an initial brief summary of the redox principle, the main reports and the activity they describe have been listed, with one or two minor exceptions, historically.

Over the past twenty years several new systems for electrochemical energy storage have been investigated [1, 2]. For some of the systems such as redox-flow batteries, development has now reached the post-prototype stage.

The redox-flow battery differs from the usual storage battery in that the energy-bearing chemicals are not stored within the battery container, but are in a separate liquid reservoir(s).

The system is very simple (Fig. 1); it consists of two tanks, each containing an active species in different oxidation states. Each fluid passes in a half-cell (a membrane divides the entire cell) and is returned to the reservoir. In the half-cell there is electrochemical exchange with the electrodes which permits the output or input of current, for example,  $Fe^{3+} + e = Fe^{2+}$ and  $Cr^{2+} - e = Cr^{3+}$ . Usually the four species (ions) are in solution and sometimes gaseous elements are involved.

In other cases metallic species are deposited in one half-cell. Such systems are referred to as being "hybrid" or "redox-hybrid".

In 1971, Ashimura and Miyake published in *Denki Kagaku* (in Japanese), a paper dealing with the polarization characteristics of redox type fuel cell cathodes at a flow-through porous carbon electrode [3]. Later they also studied the regeneration of Fe(III)/Fe(II) catholyte in the sulphuric acid of a redox-type fuel cell, and the polarization characteristics of a redox-type fuel cell cathode at a flow-through porous carbon electrode [4, 5].

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Fig. 1. Electrically rechargeable redox-flow cell.

In 1973 NASA (National Aeronautics and Space Administration, U.S.A.) founded the Lewis Research Center at Cleveland, Ohio, U.S.A. with the object of researching electrically rechargeable redox flow cells.

NASA also placed development contracts with Exxon Company (Linden, NJ, U.S.A.) [6], Giner Ind. (Waltham, MA, U.S.A.) [7], and with Gel Inc. (Durham, NC, U.S.A.) for the hybrid version, and with Ionics Inc. for membrane development.

The attractive features of an electrically rechargeable redox flow system are:

(a) simple electrode reactions,

(b) favorable exchange currents (for some redox couples);

(c) no high temperatures required;

(d) no cycle life limitations (for the redox couples);

(e) electrochemically reversible reactions (some redox couples);

(f) very high overall energy efficiency.

Their main disadvantage is a low energy density in comparison with the more usual secondary battery systems.

#### 1973

From 1973, for at least 6 years, the Lewis Research Center produced several reports in this field, covering the topics:

(i) screening of redox couples;

(ii) electrochemical diagnostics;

(iii) kinetic problems;

(iv) membrane development;

(v) electrodes (graphite, graphite felt, reticulated vitreous carbon, carbon foam, carbon cloth;

(vi) component screening and life testing;

(vii) system studies;

(viii) hydrodynamics;

(ix) models;

(x) electrocatalysis.

The reports included an electrically rechargeable redox flow cell [8]; electrochemical behavior of  $0.2 \cdot 0.3$  M ferrous chloride-ferric mixtures on edge-on pyrolitic graphite rotated disk electrodes [9]; redox flow cell development and demonstration project — calendar year 1976 report — [10]; the redox flow system for solar photovoltaic energy storage [11]; factors affecting the open-circuit voltage and electrode kinetics of some iron/ titanium redox flow cells [12], and redox flow batteries [13], by Thaller, Gahn, Miller and others. Many elements were tested, titanium (Ti<sup>3+</sup>/TiO<sup>2+</sup>), iron (Fe<sup>2+</sup>/Fe<sup>3+</sup>), chromium (Cr<sup>2+</sup>/Cr<sup>3+</sup>). Of these, the iron-chromium system,

 $Fe^{3+} + Cr^{2+} \rightleftharpoons Fe^{2+} + Cr^{3+}$ 

seemed to be the most promising for the global reaction and much effort was expended in this direction.

During this period we also find contributions from Beccu (Battelle Institute, Geneva, Switzerland) [14], who examined the redox systems with regard to secondary batteries, Warshay, who estimated the costs of electrochemical energy storage [15], Weaver — The G.E.L. iron redox cell: a report of initial cycling tests — [16], and from Zito (The iron-redox battery in a large solar-photovoltaic application) [17].

#### 1979

Roy and Kaplan (Oak Ridge National Laboratory, Tenn., U.S.A.) analysed the performance capabilities of redox-flow storage in 1979 [18]. In this period there were also some NASA patents on electrically rechargeable redox flow cells [19], on gels as battery separators [20], and on an electrochemical cell for rebalancing a redox flow system [21].

The characteristics of a "soluble" iron/titanium battery system were studied by Savinell *et al.* (Department of Chemical Engineering, Pittsburgh, Penn., U.S.A.) [22], while improvements in redox flow cell storage systems are proposed by Thaller for NASA [23, 24].

Roberts (Mitre Corporation, McLean, VA, U.S.A.) reviewed the status of the Department of Energy program on Electrochemical Storage Systems in a report issued in August 1979 [25].

#### 1980

In early 1980 a patent was granted to the Italian O. De Nora Electrochemical Plants (Milan, Italy) on an electric storage battery [26] and another to Giner Inc. on catalyst surfaces for the chromous/chromic redox couple [27] in the iron-chromium flow cell.

Some evaluations of redox systems (chromium and titanium) were made by Nozaki and coworkers [28] of the National Electrotechnical Laboratory (Tokio, Japan). The G.E.L. Inc. was granted a patent on the iron hybrid flow cell [29].

A new report from NASA [30] described a redox system based on Fe and Cr chlorides redox couples. A little later NASA was granted a patent on gels as battery separators for soluble electrodes [31] and another concerning improvement and scale-up of the NASA redox storage system (up to 1 kW) [32].

## 1981

In 1981 NASA presented a pre-prototype redox storage system, based on iron-chromium, for a photovoltaic stand-alone application [33].

Some contribution was made by the University of Akron (OH, U.S.A.) when Savinell investigated factors affecting the performance of the ironredox battery [34], the enhancing performance of the titanium(III)/ titanium(IV) couple for redox battery applications [35], and also evaluated a hybrid redox-halogen (Cr-chlorine) for use in an energy storage device [36].

Chen (Department of Chemistry, Austin, TX, U.S.A.) published work on redox couple iron(III)-iron(II) complexes with *o*-phenanthroline [37].

In February 1981, an extensive report was prepared by Nanis (Electrochemistry Group, SRI International, U.S.A.) for the Electric Power Research Institute (Palo Alto, CA, U.S.A.). This concerned work which was presented at a workshop on electrodes for flowing solution batteries at Tampa, FL, U.S.A., in November 1979 [38].

A theoretical study, comparing flow-through and flow-by porous electrodes for redox energy storage, was published by Trainham and Newman (Department of Chemical Engineering, Berkeley, CA, U.S.A.) [39]. Also in 1981 Dol signed a French patent on redox batteries with couples of iron and manganese ions [40].

Advances in membrane technology for the NASA redox energy storage systems were studied by Ling of Lewis Center [41].

Stalnaker (NASA) presented a report in which he described stacks, each consisting of forty active cells, for a 1 kW pre-prototype system (Fe-Cr) [42].

A report from Italy by Buzzanca (Cise, Milan, Italy) analyzed redoxflow batteries [43]. Hagedorn analyzed redox storage systems, in particular iron and chromium chloride redox couples, specifically for solar applications and announced the construction and testing of a 1 kW system integrated with a solar photovoltaic array [44].

## 1982

In January 1982, two Japanese patents by the Agency of Industrial Sciences and Tchnology were issued. The first was for a manganese (cathode)-chromium (anode) system [45]. The second was for chromium or titannium coupled with bromine, for which a battery output of 0.9 V at 10 mA  $\rm cm^{-2}$  was claimed [46].

Nozaki and coworkers (Energy Division, Electrotechnical Laboratory, Ibaraki, Japan) presented test results and scale-up of systems containing  $Fe^{2+}/Fe^{3+}-Cr^{2+}/Cr^{3+}$  and a screening of over forty types of carbon fibers as a potential cathode material [47].

In a report by Roberts (279 pp.) on the status of the DOE battery and electrochemical technology program, redox and Zn-Br batteries were reviewed [48].

Giner Inc. presented data at the Dechema meeting in 1982, in particular the development of  $Cr^{3+}/Cr^{2+}$  redox reactions in the iron-chromium battery [49]. Savinell *et al.* described the operating performance of an iron-titanium stationary redox battery in the presence of lead [50].

Catalytic electrodes (ZrC electrodes) for redox flow cell energy storage devices were studied by Yang [51] of the Department of Energy, Brookhaven National Laboratory (New York, U.S.A.).

Oei, a researcher of the Ford Motor Company (Dearborn, MI, U.S.A.), published exploratory experiments with redox cells utilizing  $VO_2^{1+}/VO^{2+}$ - $Sn^{2+}/Sn^{4+}$ ;  $VO_2^{1+}/VO^{2+}-Fe^{2+}/Fe^{3+}$ ;  $VO_2^{1+}/VO^{2+}-Cu/Cu^{2+}$  redox couples [52].

A singular way of recharging redox batteries was proposed by Denno (Institute of Technology, NJ, U.S.A.) utilizing ocean thermal energy [53].

## 1983

An extensive report (314 pp.) on solution redox couples for electrochemical energy storage was written by Chen (University of Austin, TX, U.S.A.) [54].

A flowing electrolyte battery was presented by Butler (Sandia Laboratory, NM, U.S.A.) at the 17th IECEC (1982) [55].

At the beginning of 1983 a patent was granted to Savinell on a chrome-halogen energy storage device [56]. Nozaki continued to work on a flow-type secondary battery using  $Fe^{2+}/Fe^{3+}$  and  $Cr^{2+}/Cr^{3+}$  [57].

A patent from NASA on zirconium carbide as an electrocatalyst for the chromous/chromic redox couple appeared in 1983 [58].

A contribution to European research was made by Cnobloch (Siemens A-G, Erlangen, F.R.G.) who studied a redox battery based on  $Fe^{3+}/Fe^{2+}$  and  $Cr^{2+}/Cr^{3+}$  [59].

The development of a circulating zinc-bromine battery was described by Bellows (Exxon Research, Linden, NJ, U.S.A.) [60].

At the 18th I.E.C.E. Conf. Nozaki described a 1 kW redox-flow battery of 96 bipolar cells for which seventy varieties of carbon fiber electrode materials had been screened [61]. At the same meeting Gahn discussed a small cell using mixed reactant solutions at 65  $^{\circ}$ C, with a chromium electrode catalyzed with Bi or Bi-Pb [62]. Butler and coworkers (Sandia Laboratory, Albuquerque, NM, U.S.A.) presented an evaluation of zinc-bromine prototype batteries [63].

Studies of the iron-chromium redox cell, and the development of an efficient electrode for  $Cr^{3+}/Cr^{2+}$  redox reactions were presented by Giner (Giner Inc., Waltham, MA, U.S.A.) [64].

A mathematical model of NASA's redox flow cell was described by Watts and Fedkiw (Department of Chemical Engineering, Raleigh, NC, U.S.A.) [65].

Iron-titanium redox and hybrid iron secondary batteries was the title of a report by Bartolozzi and coworkers (Department of Chemical Engineering, Pisa, Italy) [66].

## 1984

An improved mathematical model of the iron-chromium redox battery was made by Fedkiw. This was based on the porous electrode theory and incorporates redox kinetics, mass transfer, and ohmic effects, as well as the parasitic hydrogen reaction which occurs in the chromium electrode [67].

Nozaki again described the constructed and tested 1 kW system [68].

Yeo (Pinnacle Institute, Cupertino, CA, U.S.A.) analysed the economics of redox cells including Zn-Cl, Zn-Br, H-Cl, H-Br, Fe/Cr redox, Fe/Fe redox, Zn/ferricyanide redox, acid Fe/Zn redox and Cr/Cl [69].

Fouling mechanisms of separator membranes for the iron-chromium redox battery have been discussed by Assink (Sandia Lab., Albuquerque, NM, U.S.A.) [70]. Bartolozzi and Marconi presented an experimental study using a model of an iron hybrid cell [71].

A review, with sixteen references on redox batteries for solar energy storage, was prepared by Ritchie (Department of Chemistry, Nedlands, Australia) [72].

The discharge performance of the titanium/iron redox flow system was studied by Wang (Department of Chemical Engineering, Hsinchu, Taiwan) [73].

Nozaki presented a description of the complete system (tanks, pumps, piping and flow-control units) of the 1 kW cell using iron-chromium electrolytes [74].

Many prototypes, zinc/bromine; redox; zinc/ferricyanide flowing electrolyte batteries and cells, were discussed by Butler at the 1984 I.E.C.E. Conf. [75]. At the same meeting Nozaki also gave more information on his unit consisting of thirty bipolar cells with an electrode area of 3000 cm<sup>2</sup> [76]. A patent relating to redox batteries, including bromine and chromium, was granted to Giner (Electric Power Research Institute Inc., U.S.A.) [77].

Voltage drop and electrical resistivity measurements of ion-exchange membranes used in redox-flow batteries were studied by Ohya (Faculty of Engineering, Yokohama, Japan) [78].

Remick (Institut of Gas Technology, U.S.A.) patented a cell using sulfide-polysulfide as anolyte and chloride-chlorine as catholyte [79].

Reactivation of complex compounds by amines participating in the redox reaction was the subject of a German patent by Cheng and Reiner [80].

## 1985

The problem of reactivation in iron-chromium redox cells was investigated by Cheng (Institute of Chemistry, Peking, Peoples' Republic of China) and coworkers [81].

A general energy balance for battery systems was described by Bernardi and Newman (Department of Chemical Engineering, Berkeley, CA, U.S.A.) [82].

Sumitomo Electric Industries (Japan) patented a general system of redox flow batteries [83], with a separator consisting of a cation-exchange membrane, in January 1985.

Cheng and Hollax patented an iron-chromium type redox battery using thallium and gold for electrocatalytic acceleration of the processes [84]. Siemens A-G (F.R.G.) patented a redox cell (iron-chromium) with graphite electrodes catalyzed with gold and lead [85]. The chromium complex in the Fe-Cr redox energy storage system was identified by Johnson (Department of Chemistry, Spring Arbor, MI, U.S.A.) [86].

The Mitsui Engineering and Shipbuilding Co. Ltd. (Japan) patented a system for the determination of the state-of-charge of a redox battery [87] and general techniques for the construction of a redox cell [88].

The status of storage battery development and potential applications was studied by Mathur (Institute of Electrochemistry, Karaikudi, India) [89].

Ohya (Faculty of Engineering, Yokohama, Japan) published studies involving factors influencing the electrical resistivity of anion exchange membranes used in a redox-flow battery [90]. Mitsui patented some redox batteries containing Fe, Cu, Sn, Ni or halogens [91].

A study of the vanadium(II)/vanadium(III) redox couple for flow cell application was made by Sum (Department of Chemical Engineering, Kensington, Australia) [92].

At the 20th I.E.C.E.Conf, Miami, CA, U.S.A., August, 1985, Kanazashi (Meidensha Electrical Mfg. Co. Ltd., Tokyo, Japan) discussed the performance of a 1 kW Zn-Br battery [93].

The cycling performance at 65  $^{\circ}$ C of the iron-chromium redox energy storage system was investigated by Gahn (Lewis Center, NASA, Cleveland, OH, U.S.A.) [94].

Results of research and development of a 10 kW-class redox flow battery were presented by Mitsui [95].

The iron-chromium (graphite electrodes) redox battery was studied by Aldaz (Department of Chemistry, Alicante, Spain) [96]. The Sumitomo Electric Industries Ltd. (Japan) patented a redox-flow battery with cylindrical electrodes constructed from porous carbon fibers [97]. The preparation of redox-flow battery electrolyte [98] was patented by Mitsui.

New diaphragm membranes for redox-flow batteries were prepared by Oya (Asahi Glass Co. Ltd., Japan) [99].

An investigation of the vanadium(V)/vanadium(IV) system for use in the positive half-cell of a redox battery was made by Sum and coworkers [100].

Three Sumitomo (Japan) patents appeared in the second half of 1985. The first was for a redox-flow battery with new, flexible electrodes made from metal wires coated with carbon or graphite and embedded in conductive rubber [101]. The second patent described a redox flow system with pipeline made from plastic having low oxygen permeability [102]. In the third patent a nonionic surfactant was added to the catholyte and anolyte, thus increasing the charge-discharge efficiency [103].

Many patents were also granted to Mitsui in this period. These included a secondary Fe-Cr battery with a heat pump between the two electrolyte tanks [104]. A second patent was for iron-chlorine and tin-chlorine batteries [105], while a third described a new design of iron-chromium redox battery with the chambers filled with carbon cloth and carbon sheet electrodes [106].

Kinoshita discussed separator technology for electrochemical applications [107].

Studies of the reaction mechanisms in batteries developed at the Industrial Electrochemical Laboratory of Kyoto University (Japan) were described by Takehara [108].

A flow redox system utilizing iron-chromium couples and allchromium electrolytes was described by Doria (Department of Physics, Madrid, Spain) [109]. A redox cell containing couples of vanadium and molybdenum ions was studied by Kummer (Ford Motor Company, Dearborn, MI, U.S.A.) [110].

### 1986

In early 1986 Sumitomo Electric Industries patented a new electrode consisting of a porous carbon grid, an expanded graphite layer, and a graphite current collector for the redox-flow Fe-Cr battery [111]. Two weeks later Sumitomo described both the structure of an Fe-Cr redox-flow battery with carbon-cloth electrodes and a polypropylene film separator [112], and an alternative separator irradiated by an electron beam [113].

Methods and apparatus for rebalancing a redox flow cell system were patented by Gahn (NASA) [114].

A redox-flow battery with carbon cloth electrodes heated in an autoclave at 100  $^{\circ}$ C was described by Kondo (Sumitomo Electric Industries, Japan) [115]. A method of monitoring an Fe-Cr couple was described in which the analyte and catholyte are by-passed to a sensing cell [116].

A new all-vanadium redox flow-battery was presented by Skyllas-Kazacos [117].

Nozaki (Mitsui) reported studies of a secondary redox-flow battery (hybrid) with chromium and halogen couples showing a voltage of 1.2 V [118]. Factors affecting the design and operation of redox batteries were examined by Mosley (Department of Industrial Sciences, Lower Hutt, New Zealand) in a review with twenty references [119].

Swette (Giner Inc., Waltham, MA, U.S.A.) studied the characterization of a gold electrocatalyst for iron-chromium redox batteries [120].

At the 21st I.E.C.E.Conf., Izawa and Kondo (Chiba Laboratory and Mitsui Company, Chiba, Japan) described a 10 kW-80 kW h iron-chromium redox-flow battery stack for load-leveling, with a cell rebalancing system in which bromine is added to the electrolyte and reacts with hydrogen evolving from the negative electrode [121].

Yoshitake (Mitsui) patented an iron-chromium battery with anolyte containing Pb and Bi [122].

Mass transfer and current distribution in a zinc-redox flow cell were studied by Wu (Department of Chemical Engineering, Chicago, IL, U.S.A.) [123].

Hamamoto (Mitsui) patented a redox flow cell (Fe-Cr) with iodic acid being used to reduce Fe(III) in the analyte [124].

Electrode frames for stacked redox-flow batteries were patented by Yamamoto (Meidensha Electric Mfg. Co. Ltd., Japan) [125].

An apparatus for the determination of active-mass concentration in a redox-flow secondary battery was patented by Mori (Sumitomo) [126]. Four patents were granted in December 1986 to Sumitomo Electric Industries for electrode current collectors for redox-flow batteries [127 - 130].

Butler (Sandia Laboratories, Albuquerque, NM, U.S.A.) subjected prototype Zn-Br; Zn-ferricyanide; iron-chromium couples to baseline tests to determine stable operating conditions [131].

The resistivity of ion-selective membranes for redox-flow batteries was calculated by Ohya (Department of Chemical Engineering, Yokohama, Japan) [132].

1987

A process for reactivating a completely discharged redox battery was patented by Ledjeff [133].

Exchange current densities of the  $Fe^{2+}/Fe^{3+}$  couple were studied by Mathur (Electrochemical Institut, Karaikudi, India) [134]. The Fe-Cr redox-flow battery prototypes, having graphite plates with baffles to promote turbulent flow of the electrolyte, were studied by Climent and Garces (Department of Chemistry, Alicante, Spain) [135, 136]. Apparatuses for electrolyte regeneration of redox flow batteries were patented by Shigematsu (Sumitomo, Japan) [137].

New processes for the manufacture of redox-flow battery electrolytes were patented by Kaneko (Japan Metals and Chemicals Co. Ltd.) [138].

The shunt-current in a redox-flow battery stack was numerically analyzed by Kanari [139] using a simple equivalent circuit model.

An analysis of electrolyte-circulating secondary batteries was made by Mori for Sumitomo [140].

Electrode material for redox-flow batteries, in particular sheets of carbon-fiber cloth, were analyzed by Kitanaka (Toray Industries Inc., Japan) [141].

Hydrophilic and porous film separators for redox-flow batteries were studied by Shigematsu (Sumitomo Ltd.) [142]. Microbe regeneration of a redox-flow battery catholyte was patented by Tsunoda [143].

Licht (Weizmann Institute of Sciences, Rehovot, Israel) studied a half-cell for electrochemical storage utilizing the high aqueous solubility of potassium polysulfide [144]. Cnobloch (Siemens A.-G., Erlangen, F.R.G.) described an Fe-Cr redox-flow battery using a new electrode catalyst to reduce hydrogen, and having a power output of 17 W, at the Dechema Congress [145].

New electrolytes for the Cr-Fe redox-flow battery were investigated by Kaneko (Kawasaki Heavy Industries Ltd., Japan) [146]. Diaphragms for redox-flow batteries were studied by Shigematsu (Sumitomo Ltd.) [147].

The performance of an all-vanadium redox flow cell with carbon felt electrodes and cation selective membrane was described by Skillas-Kazacos [148].

An advanced 10 kW Fe–Cr redox-flow battery was described by Kamio (Chiba Laboratory, Mitsui Engineering, Chiba, Japan) at the 22nd I.E.C.E. Conf. [149].

### 1988

New characteristics of an all-vanadium redox flow battery were described by Rychcik in early 1988 [150].

Some ion-exchange separator modifications for redox-flow batteries were patented by Yamamoto (Tokuyama Soda Co. Ltd., Japan) [151].

A 10 kW Fe-Cr redox battery with an 80% energy efficiency and 300 life cycles has been described by Shimizu (Kansai Electrical Power Co., Amagasaki, Japan) [152]. A 10 kW, Fe-Cr redox flow battery was also studied by Hoshitake (Mitsui Eng., Ichihara, Japan) [153].

The application of conductive organic polymers (polyacetylene and polypyrrole) to battery electrodes was reviewed by Duic (Technology Faculty, University of Zagreb, Yugoslavia) [154].

A general evaluation test of four advanced 10 kW batteries (Na-S; Zn-Cl; Zn-Br; redox-flow Fe-Cr) was made by Takahashi (Industrial Research Institute, Osaka, Japan) [155].

The reversibility of  $Fe^{3+}/Fe^{2+}$  systems in various carbonaceous materials was studied for redox battery applications by Climent (University of Alicante, Spain) [156].

An iron-chlorine redox system with graphite cloth gas electrodes was studied by Kondo (National Chemical Laboratory, Tsukuba, Japan) [157, 158].

Electrolytes for redox-flow batteries, prepared from ferrochromium ores, were patented by Wakabayashi (Chiyoda Chemical Engineering Co. Ltd., Japan) [159].

A redox-flow battery (Fe-Cr) incorporating a catholyte-reactivation process was patented by Yamanochi (Sumitomo, Japan) [160].

The preparation of carbon-fiber electrodes for Fe-Cr redox flow batteries was described by Iizuka (Toyobo Co. Ltd., Japan) [161].

Redox-flow batteries with polymer grafted surfaces and a hydrophilic monomer separator were described by Yamanochi (Sumitomo, Japan) [162].

New cation-exchange membranes to be used as separators in redoxflow cells were prepared by Yamamoto (Tokuyama Soda Co. Ltd., Japan) [163, 164].

The performance of a diaphragm-type iron-chromium redox flow cell was studied by Sawai (Faculty of Engineering, Okayama, Japan) [165].

Heat storage by redox-flow battery aqueous solutions was studied by Sekiguchi (Ebara Corp., Japan) [166].

Some electrolyte volume changes during constant-current cycles of a diaphragm-type iron-chromium redox battery were observed by Sawai [167].

A new structure for circulating electrolyte and electrolyte-distribution useful for redox-flow batteries was patented by Shimuzu (Kansai Co. and Sumitomo Ltd., Japan) [168].

A method for re-balancing redox-flow batteries using u.v. radiation was described by Hamamoto (Mitsui Ltd., Japan) [169].

Operations involving the catholyte and anolyte circulation rates (in a 10 kW Fe-Cr redox-flow battery) to save energy, and a method of rebalancing were described by Nakamura (Mitsui Ltd., Japan) [170, 171].

A review of secondary batteries (including redox and redox-hybrid) was made by Mennicke (Brown Boveri, Heidelberg, F.R.G.) [172]. New electrolyte supply operations in redox-flow batteries were patented by Hatta (Mitsui, Japan) [173].

Shunt-current eliminators for redox-flow batteries were described by Okamoto (Nippon Kokai K.K., Japan) [174]. The evaluation of membranes for an all-vanadium redox cell was made by Grossmith and Skyllas [175].

A new structure for fuel cells, redox-flow batteries, and electrolytic cells was patented by Sekiguchi (Ebara Corp., Japan) [176]. Experiences

with Fe-Cr redox-flow batteries were described by Izawa (Mitsui, Japan) [177].

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