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A MICROPROCESSOR-AIDED MODIFIED SIMONS' REACTOR SYSTEM FOR ELECTROCHEMICAL FLUORINATION PROCESSES

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SUMMARY

A modified Simons' reactor system has been developed for electrochemical fluorination processes. This reactor employs batch mixer design criteria to enhance and enable the characterization of the mass transfer in the reactor. Four monopolar packs of electrodes, each comprised of two nickel anodes sandwiched between three nickel cathodes, were used. A more uniform anodic current density distribution was achieved and the electrode packs were oriented to serve as baffles for the mixed flow field.

A custom designed and fabricated, Motorola 6800 based, microprocessor system in conjunction with an IBM Personal Computer and other accessories are employed for data acquisition, monitoring and control of the process.

The uniqueness of the design and operational characteristics of this microprocessor-aided modified Simons' Reactor System will be discussed.

INTRODUCTION

Electrochemical fluorination (ECF) processes have been investigated using various electrode configurations, e.g. reactors with a hollow anode [1,2], a porous anode [2], and a rotating cylindrical anode [2] have been used. However, the majority of reactors for ECF studies employ a pack of alternating anode and cathode sheets immersed in a common anhydrous hydrogen fluoride (AHF) electrolyte [1-4]. Reactors with this electrode configuration are generically referred to as Simons' cells, in reference to the design used by Simons' in his pioneering work on the ECF process

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[5]. Typically, the Simons' cell does not employ membranes or other separators, except for mechanistic investigations [6]. Agitation in the Simons' cell is achieved by gas evolution and electrolyte boiling through the vertically oriented electrodes or provided by a mechanical stirrer. The major concern in the design of the Simons' cell is the maximization of the ratio of electrode surface area to electrolyte volume while maintaining an adequate electrode spacing.

The Simons' cell does perform adequately for many ECF studies and its scientific and commercial importance is well recognized. Nevertheless, improvement in the design is possible and may lead to an enhancement of the ECF process. Additionally, the advancement of computer technology in recent years provides an opportunity to more closely monitor and control the process. This combination should lead to improved results and a better understanding of the process.

This paper describes the design of a modified Simons' reactor which has improved mass and heat transfer characteristics and a more uniform anodic current density distribution. The reactor and supporting components are automated with a distributed microprocessor-aided control and data acquisition system. In addition, a description of the supporting units, including the safety features, is presented to provide a complete picture of a unique ECF system.

DESIGN OF THE MODIFIED SIMONS' REACTOR

The improvement of the current density distribution on the anode, the bulk mixing, and the mass and heat transfer characteristics are the objectives of this modification of the reactor design.

Current Density Distribution

The Simons' reactor employs an evenly-spaced monopolar pack of two anodes and three cathodes arranged in an alternating fashion. The current distribution on any electrode surface facing another electrode is quite uniform, except very near the edge as shown in Figure 1(a). The current distribution on the outside face of a terminal electrode in a pack is very non-uniform as it faces no electrode of opposite polarization as shown in Fig. 1(b). Figure 1 is obtained by numerical solution of the Laplace equation for the primary current density distributions on an electrode with the same width-to-gap ratio (3.2 cm by 0.32 cm) as those employed in the modified Simons' reactor. Since the anode is the electrode at which the fluorination reaction occurs, it is desirable to maintain the anodic current distribution as uniform as possible. To achieve this, the modified Simons' reactor uses an electrode pack in which the two anodes are sandwiched between three cathodes in a monopolar arrangement.

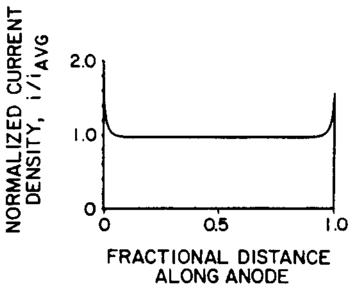

Figure 1(a)

Fig. 1(a). Primary Current Density Distribution on an Anode

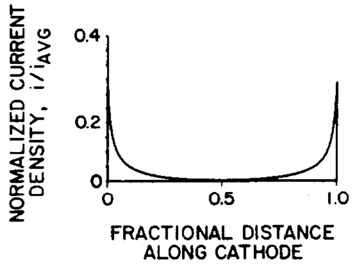

Fig. 1(b). Primary Current Density Distribution on the End Cathode

Bulk Mixing

The electrode arrangements and the symmetry of the flow field in the modified Simons' reactor are shown in Fig. 2. Conventional batch mixer design principles [7-12] are used for two reasons. First, the symmetry of this design provides uniform agitation in the fluid bulk at various scales of agitation [11]. Second, this geometry permits scale changes while preserving the magnitude of agitation [12], simplifying scale-up

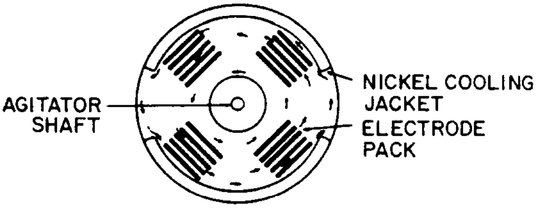

Fig. 2. Flow Field in the Modified Simons' Reactor

considerations and permitting comparisons of data obtained in reactors with similar geometries.

In a cylindrical flow field, vortexing can occur at high agitation rates. One method to prevent vortexing employs baffles located every 90 degrees along the wall. In order to minimize the possibility of stagnant pockets forming around the electrodes, the packs are rotated 90 degrees from the baffle's normal orientation to the wall. This permits the region between the electrodes to be swept by the circumferentially flowing electrolyte. In this manner, each of the four electrode packs serve as a baffle while the flow field and the diffusional boundary layer in the vicinity of each anode should be similar.

Mass Transfer

The mass transfer across the diffusional boundary layer on the anode is of interest in this study. A dimensionless correlation of the global mass transfer to the level of agitation is given by:

$$Sh = a(Sc)^{1/3} (Re)^{b} \qquad (1)$$

Where Sh = Sherwood number; the dimensionless rate of mass transfer

$$= \frac{Ir}{AnFDC_{\infty}}$$

Re = Reynolds number; the dimensionless agitation rate = $\omega r^2/\nu$

Sc = Schmidt number; the dimensionless ratio of convection to diffusion = ν/D

I = total reactor current, in amperes
r = radius of the agitator impeller, in cm
A = total electrode surface area, in cm^2
D = diffusion coefficient for the reactant, in cm^2/sec
C^{∞} = bulk concentration of the reactant, $g\text{-}mole/cm^3$
ω = rotational speed of the agitator, rad/sec
ν = kinematic viscosity of the electrolyte, cm^2/sec

The values of the constants a and b in equation (1) are determined empirically and are specific to the flow regime and system in which they are obtained. Typically, a Sherwood number dependence on the Reynolds number to the 0.6 to 0.8 power is found for turbulent flow. Experimentally, limiting current techniques [13-17] can be used to obtain the values of a and b, and consequently, the mass transfer characteristic for the reactor system. The characterization for this system will be given later.

EXPERIMENTAL

Using the design criteria mentioned above, a modified Simons' reactor was fabricated with TFE Teflon. Figure 3 shows the top view of the reactor and Fig. 4 the side view.

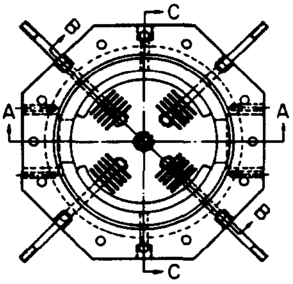

Fig. 3. Top View of the Modified Simons' Reactor

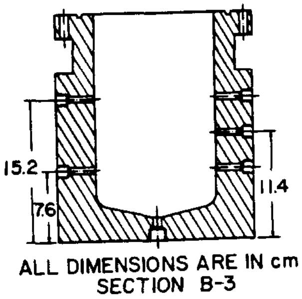

Fig. 4. Cross-Sectional View of the Modified Simons' Reactor

The reactor has a total volume of ∿1500 cm^3. Other than the electrodes ∿1 and the thermowell, the only metallic components in contact with the AHF electrolyte are the nickel cooling jackets. All anodes and cathodes are fabricated from 0.159 cm thick Nickel 200 sheet, 99.5% nickel (International Nickel Company, Inc.). The total anodic surface area is 620 cm^2 and the total cathodic surface area is 930 cm^2. A centerline-mounted pitched blade agitator, coupled to a custom-built variable speed controller is used to obtain desired level of agitation. The reactor has four illuminated FEP Teflon portholes for visual observation. Additional ports are available for reactant addition, sample removal, electrode connections, thermowell, overpressure blowout and gas inlets and outlets.

The mass transfer characteristics of this reactor were determined with the limiting current technique using the well-studied ferro/ferricyanide redox couple. During ECF, the electrochemical reaction of interest occurs on the anodes, and it was for these electrodes that the mass transfer was characterized. A 1 M NaOH solution was used as a supporting electrolyte to minimize the ohmic effects. The second and fourth electrodes in each pack, which would be anodes during ECF, were potentiostated cathodically for the mass transfer characterization. This utilized the wide limiting current plateau for the reduction reaction in alkaline ferro/ferricyanide solutions. A platinum wire, 0.013 cm diameter by ~1 cm length, was employed as the reference electrode and the first, third, and fifth electrodes in each pack served as the counter electrodes.

The nickel electrodes were activated at 20 mA/cm^2 in a 5% NaOH solution, as described by Alkire and Chen [17], immediately prior to the limiting current characterization. The ferricyanide concentration was 0.001 M and the ferrocyanide concentration was 0.01 M. Repeated characterizations with fresh solutions were performed and the agreement among the runs was very good as shown in Fig. 5, which displays the composite data of several runs.

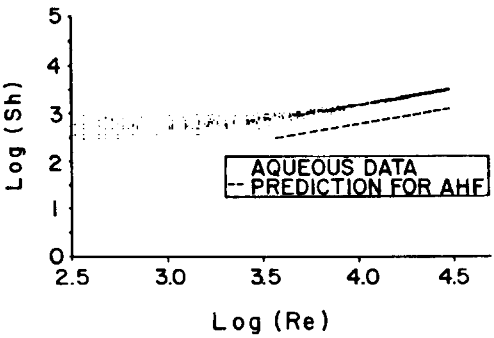

Fig. 5. Limiting Current Characterization of the Modified Simons' Reactor

The modified Simons' reactor is controlled and monitored by several custom designed microprocessors with several objectives. The reactor system can be operated at controlled cell voltage or controlled anode potential, using a Cu/CuF_2 reference electrode in the latter case. The ECF process is highly exothermic and precise control of the operating temperature is important for a kinetic study. Additionally, the control and monitoring of the agitation level and data acquisition of several other variables are of experimental importance. Thus a specialized microprocessor system is used for control, monitoring and data logging for the modified Simons' reactor. The data acquisition system consists of two custom-built microprocessors (Motorola 6800 based), a Hewlett-Packard 2641A terminal, a Hewlett Packard 1332 X-Y display, a Houston Instruments Omniscribe strip chart recorder and an IBM Model 5150 Personal Computer. This data acquisition system is located outside of the room containing the experiment, a 3 meter by 3 meter steel-reinforced concrete cell block.

A block diagram of the data acquisition system is shown in Fig. 6. The IBM PC serves as the destination of the data which is stored on floppy diskettes. Through specifically developed software, the IBM PC monitors the progress of the experiment and is capable of terminating the experiment if an abort condition occurs in a monitored parameter. It is possible to change the set point of the potentiostat or agitator controller etc., either from the IBM PC or from the Hewlett Packard terminal. The system can monitor up to 44 parameters simultaneously and reports them at 5 second time intervals. At a sampling rate of 1 data set per

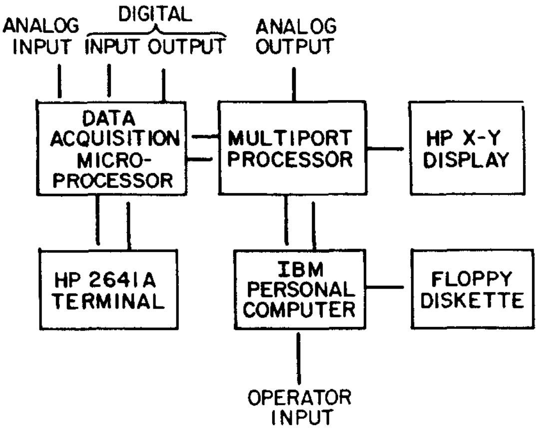

Fig. 6. Block Diagram of the ECF Data Acquisition System

minute with 8 data channels recorded, over a week's worth of data (360 KB) can be stored before it is necessary to change diskettes.

The modified Simons' reactor and the microprocessor-aided control and data acquisition system represent the essential elements of the ECF system. There are, however, other components of the system which merit mention. Figure 7 shows a simplified schematic of the system. High purity nitrogen gas is dessicated and passed into the system as a constant purge. The nitrogen first passes through a knockout drum, inserted as a safety precaution to provide flow capacitance, and then enters the reactor and passes over the AHF electrolyte. In this manner, volatile products are continually removed from the reactor for safety reasons. An auxillary nitrogen feed line is available for pressurized reactant addition (the reactor typically operates at ~10 kPa above ambient pressure) or backflushing the electrolyte sampling valve on the bottom of the reactor. There is a product reservoir, which is made of monel and jacketed to permit the circulation of coolant. An overflow return on the side permits the product reservoir to function as a decanter, recycling HF to the cell while collecting fluorocarbon product. Most of the HF and any fluorinated product not condensed in the product reservoir is condensed in the monel reflux condenser located above the product reservoir and following it in the flow train. Typically, both the product reservoir and the condenser are maintained at -60 C. Only low boiling fluorocarbons, nitrogen, fluorine, hydrogen, oxygen difluoride and trace amounts of HF are able to exit the reflux condenser and these gasses pass through another knockout drum before entering the aqueous traps. The aqueous traps contain potassium iodide to neutralize any powerful oxidants, e.g. OF_2 and F_2, and any HF reaching them will pass into solution. In this manner only nitrogen, trace organics and hydrogen exit the process and samples of the trap solutions may be iodimetrically titrated to determine the amount of oxidants neutralized. For safety, an auxillary overpressure blowout system, not shown in Fig.7, is attached to the reactor.

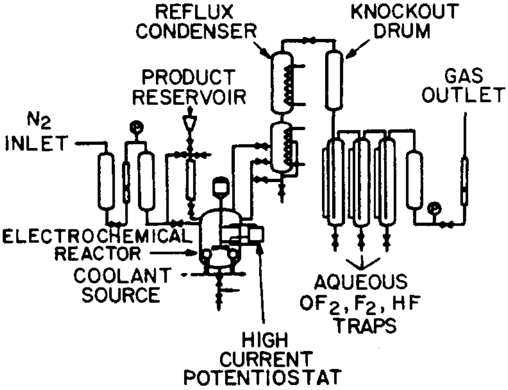

Fig. 7. Schematic of the Electrochemical Fluorination System

The reactor temperature can be maintained within 0.5 C of the set-point temperature using a time proportioning temperature controller, Omega model 807MJ. The cooling source employed is a Neslab ULT-80 cooler, capable of providing up to 13 liters of methanol coolant per minute at temperatures down to -80 C.

The potential of the anodes in the reactor is controlled versus a Cu/CuF_2 reference electrode by a custom-built high current potentiostat which is powered by a Lambda model LES-EE-02-OV power supply. The potentiostat setting may be changed remotely using the computer and can provide up to 29 amperes at 18 volts, sufficient for the ECF requirements at the conditions investigated.

In summary, the combination of the modified design and microprocessor control of this Simons' reactor provides excellent performance characteristics for the ECF system as well as for investigations of other electroorganic processes not requiring a divided cell. The applications of this system for a specific ECF study will be described in a separate publication.

ACKNOWLEDGEMENT

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