Convection in Electrochemical Systems

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Abstract. Some theoretical and experimental results for the concentration and velocity fields that appear during unsteady electrolysis in small electrochemical cells are given. Two systems are considered: $[\text{Cu} | \text{CuSO}_4(aq) | \text{Cu}]$ and $[\text{PbO}_2, \text{PbSO}_4 | \text{H}_2\text{SO}_4(aq) | \text{Pb}, \text{PbSO}_4]$. For the former system, in which the electrodes are solid, both linear and nonlinear electrode kinetics are considered. For the more complicated latter system, where the electrodes are porous, attention is restricted to linear kinetics. Theoretical results are obtained by using both perturbation methods and numerical analysis. Experimental results are obtained by Laser Doppler Velocimetry and Image Laser Holography. It is shown that the evolution of the concentration and velocity fields is controlled by stratification of the electrolyte. The boundary layer structure is similar to that appearing during nonlinear spin up of a homogeneous fluid. Theoretical and experimental results are in good agreement.

1. Introduction

In the late sixties and seventies, the Swedish government initiated a national research program for theoretical and experimental studies of the fluid mechanics of centrifugation of gaseous $UF_6$-isotopes. The aim of the program was to establish sufficient technological knowledge within the country in order to build an enrichment facility for fuel supply to the Swedish nuclear energy program, possibly in cooperation with some other European country. Mårten Landahl was one of the chief architects of this program and made several important contributions, in particular on the gas dynamics and the principal design of gas centrifuges. Much of the research was carried out under Mårten Landahl’s supervision in the Department of Mechanics at the Royal Institute of Technology. During the summers, several of his colleagues at M.I.T., Roger Gans, Louis Howard, Willem Malkus and Sherwin Maslowe, visited Sweden for participation in the program. During this period, Mårten Landahl and his colleague Sune Berndt at KTH started a series of biannual international workshops on uranium enrichment by centrifugation. These workshops, with regularly participating researchers from France, Great Britain, Italy, Japan, The Netherlands, Sweden, U.S.A., West Germany and later also the Peoples Republic of China, remained very active until the middle of the eighties when, in most countries, including Sweden, research in this area was closed down. There were several reasons for this, the public opinion, the maturity of the tech-
nology and the excess of enriched uranium available at low price on the world market. However, the most important reason was probably that considerably more successful alternative technologies emerged. As for the Swedish program, it was characterized by Mårten Landahl as "... one of those technically and scientifically very interesting programs that never led anywhere ...".

The first of the present authors had the pleasure of participating in the aforementioned research. It was a period of great enthusiasm. The field was one of both scientific and industrial interest where progress could be and was made by using analytic perturbation methods in parallel with large scale numerical computations. Also some very interesting experimental work was carried out.

Several years after the Swedish project on uranium enrichment was aborted, the first of the present authors, by mere incidence, entered another field where the physical phenomena are quite similar to those that appear in rapidly rotating flows, namely free convection in electrochemical systems. This area of research, which is a combination of electrochemistry and fluid mechanics, was rather active until the late fifties when, in spite of its significant technical importance, it simply started to fade away. The main reason for the decreased activity was probably that researchers in electrochemistry and fluid mechanics, respectively, tended to be successively more encapsulated in their own specialties as the steadily growing complexity of the two fields made simultaneous research in the two areas increasingly difficult.

The literature on the interaction between electrochemical phenomena and fluid motion is consequently quite small. The classical treatment of the subject is the book by Levich (1962). The standard reference from the electrochemical point of view is the book by Newman (1991). Some interesting recent contributions, in which fluid mechanical phenomena are of primary importance, are summarized by Probstein (1990) in a recent book.

In this paper, which addresses researchers in fluid mechanics, we give an outline of some of the basic mass transfer phenomena that are encountered in electrochemistry. Some published and some yet unpublished results, which have been obtained in collaboration with researchers in the Department of Technical Electrochemistry and Corrosion Science at the Royal Institute of Technology, are presented. The analogy with similar phenomena in the theory of rotating flows is discussed in some detail.

Some technical applications where interaction between fluid motion and electrochemical reactions are of primary importance should be mentioned. In materials science, combinations of electrochemical and fluid mechanical phenomena appear in electroplating, electrorefining and electrowinning of metals. Similar phenomena are of importance in various parts of energy technology such as charging and discharging of batteries and the operation of fuel cells. In electrolytic production of chemicals, effects of fluid motion are, in many cases, of primary importance. Another field of application is electrolytic purification of waste water and desalination of sea water. From a scientific point of view, an interesting application was pointed out by Ward III and LeBlanc (1984), who noted that experimental stud-