

Electroinitiated Polymerization Coatings Through Packed and Fluidized Bed Electrodes

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Synopsis

Our previous studies on electroinitiated polymerization for formation of coatings on metal surfaces have all been in stationary cell systems. The feasibility of using either a packed bed or a fluidized bed cell in electroinitiated polymerization is now demonstrated, the objective being to form polymeric coatings on metallic and metal-coated nonmetallic particles. The metallic particles that have been used are aluminum and stainless steel and the monomer-electrolyte system used is DAA-sulfuric acid. A comparison of current densities under various cathode potentials for the packed and fluidized bed systems is presented. The coatings obtained are analyzed through IR to establish the polymer functional groups. Additionally, both elemental analyses and thermal neutron activation analyses have been carried out to establish the compositions of the polymer coatings.

INTRODUCTION

Electrode transfer processes have, over the last few years, become useful in the development of polymeric coatings on metal surfaces. In the case of electrocoating, an already formed polymer is deposited on a metal surface through electrophoretic processes.¹ In electroinitiated polymerization, early work²⁻⁵ has been carried out with the objective of achieving polymerization within the cell solution. In our electropolymerization work reported earlier,⁶ the polymerization was initiated by electrolysis as above, but with the modified objective of depositing these polymers onto different metals to form protective films which are electrically insulating and also resisting corrosion, thus enabling practical applications for these coated metals. A stationary system involving the monomer-solvent-electrolyte solution being held in a three-compartment cell was used; the cathode and anodes were metallic plates, held immersed in the cell contents.⁷

The above work is now being extended in a new direction wherein the electroinitiated polymerization is carried out in a fluidized bed electrolytic cell with the objective of forming polymeric coatings on metallic and metal-coated nonmetallic particles. In such a system, metallic particles form the cathode, thus making available low current densities in view of a large electrode surface area per unit volume of the bed. Furthermore, the continuous disturbance of the bed contributes to the preferred high rates of mass transfer to the surface of the particle.

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BACKGROUND

Electroinitiated polymerization for development of coatings on metal electrodes and the stationary cell system used for such work are described elsewhere.⁷ However, since no published literature is available on electroinitiated polymerization in continuous flow systems involving packed and fluidized bed systems, an attempt is made here to show the logical extension of available literature on electro-organic syntheses for possible applications in electropolymerization.

A variety of continuous flow cell configurations are now available to the process designer for electro-organic syntheses. Flat plate cells, usually operated in parallel and arranged in filter-press configuration, are highly developed and simple to operate and maintain.⁸ At the present time, those receiving much attention are cells capable of providing much higher electrode surface area per unit volume than can be attained with flat plate cells. These include packed beds, fluidized beds, and pumped slurry cells.⁹ The fluidized bed and pumped slurry cells employ very fine current-conducting particles dispersed in the electrolyte solution. The emphasis in these investigations is on electro-organic synthesis, with the reactions taking place at the surface of each individual particle and the defined product coming out either in the gas phase or in the liquid phase. These cells have not hitherto been used in electroinitiated polymerization, especially for the development of coatings. It should, however, be pointed out that fluid bed methods do exist for coating particles and objects of various shapes and dimensions. The coating is by, for example, vapor deposition,¹⁰ fluid-bed pyrolysis,¹¹ melt spraying,¹² electrostatic deposition,¹³⁻¹⁵ thermal diffusion,^{16,17} electroreduction,¹⁸ plasma-jet generation,¹⁹ fusion,^{20,21} etc.

In a fluid bed cell, conducting particles are fluidized by a flowing electrolyte and charged by a current feeder which is connected to the external circuit. Because of their discontinuous nature (and depending on the hydrodynamics and electro-dynamics of the process) fluidized electrodes allow relatively uniform electrode activity on the surface of the particles. Two-phase fluidized electrodes have been used experimentally for the reduction of *m*-nitrobenzene sulfonic acid,²² the reduction of oxygen,²³ the oxidation of methanol,²⁴ and the electro-deposition of copper.^{25,26} In general, the cathodes operate satisfactorily when the bed expansion is up to 25%. For favorable cases, current concentrations from 7.5×10^{-3} to 185×10^{-3} A cm⁻³ are reported for electrode reactions in which the corresponding plane electrode current densities are from 0.1×10^{-3} to 5×10^{-3} A cm⁻².^{22,26} The electroreduction of oxygen to peroxide in both two-phase and three-phase fluid beds of carbon particles has also been investigated.²⁷ For the operation as a two-phase fluid bed, the catholyte was presaturated with oxygen while in the three-phase system, oxygen was sparged into air-saturated catholyte.

A fluid bed cathode gives high current efficiencies coupled with high-power efficiencies.²⁵ Conventional electrolysis equipment for electrowinning of copper from dilute leach liquors (CuSO₄ solution with 2 g/l. Cu) is impractical because of high-power consumption caused by concentration polarization on the cathode and consequent production of H₂ instead of Cu deposition. However, low current densities per unit cathode area favor copper deposition and prevent the rapid deposition of the Nernst layer on the cathode which causes the onset of polarization. In practice, operation of conventional equipment at such low current

densities is impractical and uneconomical. This is a situation wherein the fluid bed becomes useful in view of the availability of a large surface area of electrode per unit volume of electrode/cell. Thus, for a given total cell current, the current per unit area of the electrode is greatly decreased compared with that for the conventional plane electrode system. In industrial electrochemical cell design, the electrodes are 1 to 30 ft² ft⁻³ of cell volume—adequate for chloride ion discharge. For a current density of 100–1000 A ft⁻², the cells operate at 1000–3000 A ft⁻³. Many organic reactions occur at current densities of only 1–10 A ft⁻², i.e., the flat plate will be operated with an intensity of only 3%–10% of current practice. The higher investment necessary to offset the reduced performance of each cell becomes unrealistic. This has then led to the development of a new cell design with a higher specific area—the fluid bed electrode cell. The advantages of the fluid bed electrode cell can then be summarized as (i) large electrode surface area per unit electrode/cell volume; (ii) low current per unit area of the electrode, low current densities usually being favorable for electro-organic reactions; (iii) Continuous disturbance of diffusion layer in the electrolyte phase due to particle collision and turbulence and hence high rates of mass transfer to the surface of the particle; and (iv) absence of dendrites formation.

Similar advantages could be expected in using the above fluid bed cell for

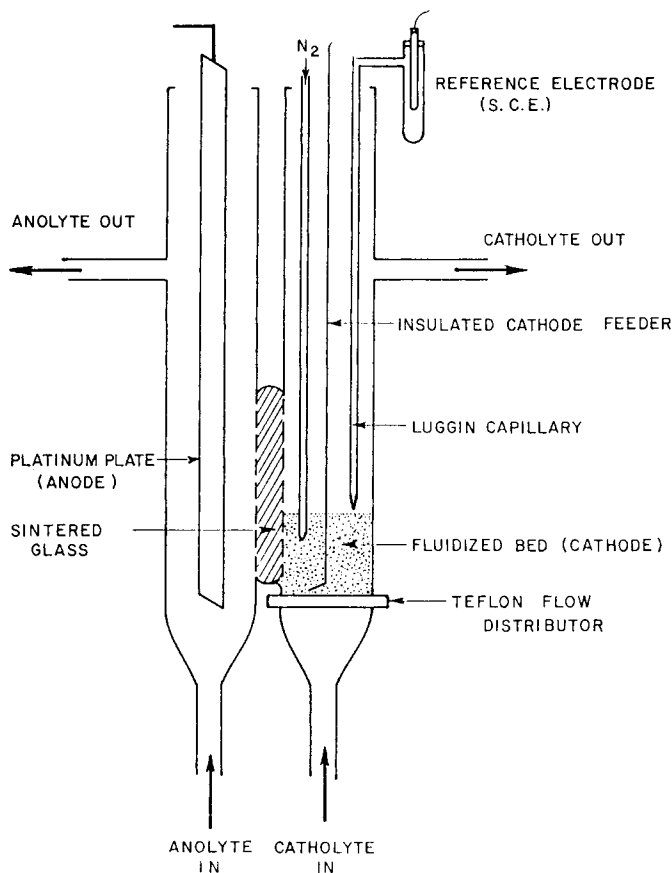


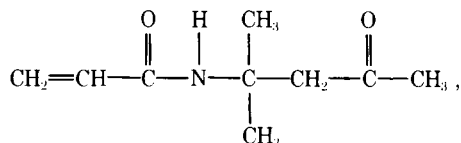
Fig. 1. Two compartment fluidized bed cell (side-by-side design.)

electroinitiated polymerization and these are shown to be feasible through the studies being carried out in our laboratories and reported herein.

EXPERIMENTAL

Materials

Colorless solid monomer diacetone acrylamide (DAA,



Lubrizon product) and 97.4% sulfuric acid (Baker) are used without additional treatment. Aluminum shots (417–590 μm , Pellets Products), aluminum plate, and stainless steel plate are first washed with distilled water and acetone and then degreased with trichloroethylene, prior to polymerization runs. The Al plate is 98.8% Al and 1.2% Mn while the stainless steel is 66%–70% Fe, 18%–20% Cr, 8%–12% Ni, 2% Mn, and 1% Si.

Electrolytic Cell and Polymerization Runs

The packed/fluidized bed consists of two glass compartments, each 21.4 mm i.d. \times 270 mm long, separated by sintered glass (Fig. 1). A platinum plate (254 \times 12.5 \times 0.5 mm) is used as the counter electrode in the anode compartment. In the cathode compartment, aluminum particles are supported on a flat, perforated

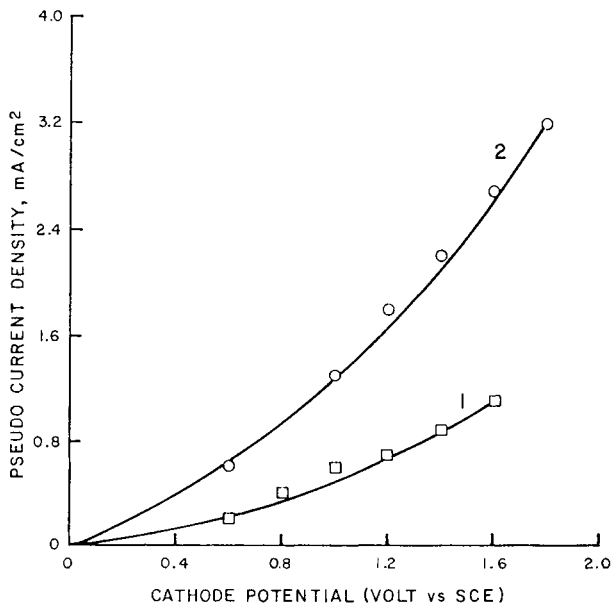


Fig. 2. Pseudo-current density vs cathode potential for the electroinitiated polymerization of DAA. (1) Packed bed electrode, $v = 0.55$ cm/sec; (2) fluidized bed electrode, $v = 3.10$ cm/sec.

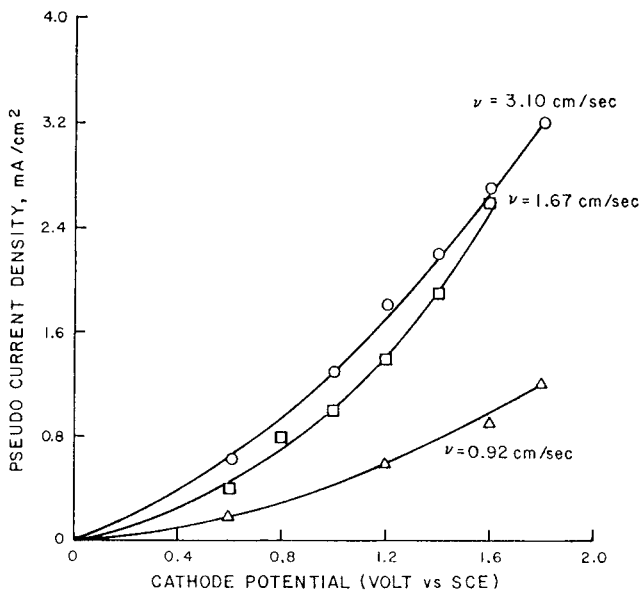


Fig. 3. Pseudo-current density vs cathode potential for the electroinitiated polymerization of DAA in a fluidized bed electrode system for various flow velocities.

teflon flow distributor, with an insulated copper wire serving as the feeder electrode. Whenever desired, the aluminum particles and the feeder electrode are replaced by a single aluminum or stainless steel plate cathode ($203 \times 12.5 \times 0.6$ mm).

A dual flow recirculation system is used during electrolysis. A 0.5M DAA solution in 0.1N H_2SO_4 is pumped through the cathode compartment, while the 0.1N H_2SO_4 electrolyte, without any monomer in it, is circulated through the anode compartment. Nitrogen is continuously bubbled through the catholyte and anolyte solutions as well as through the cathode compartment. The cathode potential is measured by a saturated calomel electrode (SCE) which is connected to the cathode compartment by a Luggin capillary. The current and voltage are continuously recorded on a potentiostatic chart recorder and the current density calculated.

Analyses

A Perkin-Elmer Model 700 IR spectrophotometer is used to establish the polymer functional groups. Elemental analyses of the polymer coating are carried out on a Perkin-Elmer Model 240 elemental analyzer. The neutron activation analyses for the metals are carried out by simultaneous irradiation with a standard sample, 5 min for Al and 8 hr for stainless steel, at the WSU TRIGA Nuclear Reactor. Activities are measured with the Ge(Li) detector.

RESULTS AND DISCUSSION

The polarization curves of pseudo current density/cathode potential obtained for the electroinitiated polymerization of DAA, using 0.1N H_2SO_4 as the supporting electrolyte in the packed and fluidized beds are shown in Figure 2. The

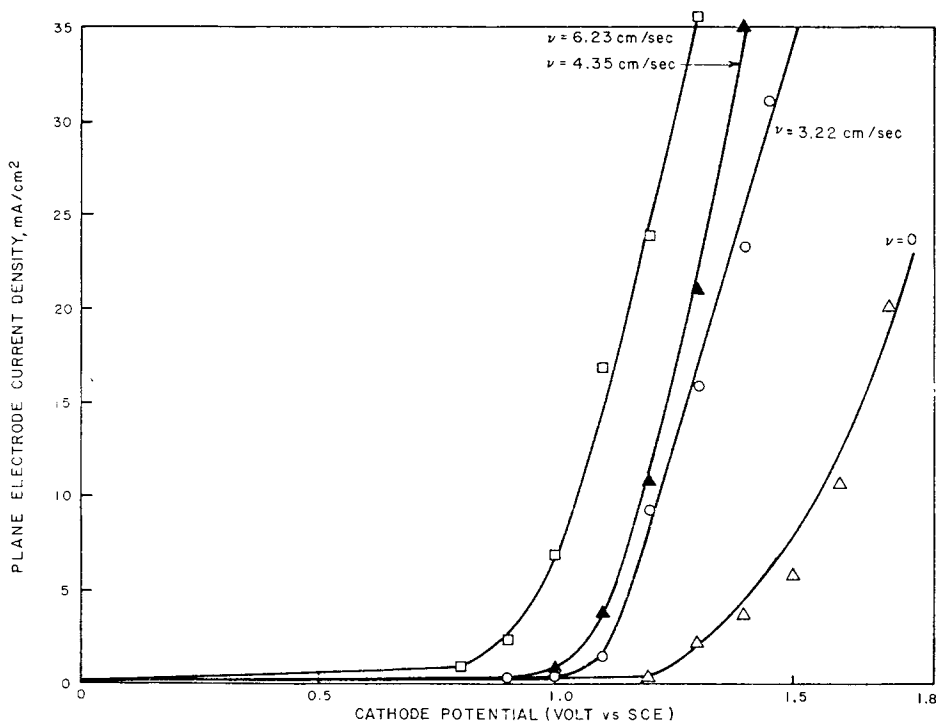


Fig. 4. Plane-electrode current density vs cathode potential for electroinitiated polymerization of DAA; aluminum plate cathode, flowing catholyte.

pseudo current density is defined as current concentration or specific current density, which is the current supported by unit volume of electrode bed,²² divided by the specific area (A) of the particles. Specific area A is

$$A = 6(1 - V)/d$$

where d is taken as the mean shot diameter and V is the voidage, determined experimentally ($V = 0.55$). Curve 1 in Figure 2 was obtained for the case of a packed bed of aluminum shots wherein a flow of solution was maintained low enough so as not to fluidize the bed; and curve 2 was obtained with the same aluminum particles, but in a state of fluidization. It is observed that the pseudo-current density in the fluidization case is higher than that for the packed bed electrode, under the same applied cathode voltage. The possible reason is explained by Kreya, Pionteck, and Hertz.²⁸ If one considers a fluidized bed electrode of conducting particles in which a diffusion-controlled electrochemical reaction takes place, one finds that the increase in pseudo current density is due to two reasons. Firstly, the effective electrode surface area and the total current are considerably higher for a fluidized bed electrode, and secondly, particle collisions and turbulence in the bed cause continuous disturbances of the diffusion layer, all contributing to a net increase in pseudo current density. Also, Hiddleston and Douglas²⁹ point out the main advantage of fluidization lies in the fact that the entire surface area of the particles could be utilized.

Figure 3 shows the pseudo-current-density-cathode-potential curves obtained, for the electroinitiated polymerization of DAA using $0.1N$ H_2SO_4 as electrolyte, in a fluidized bed electrode system under various flow velocities (i.e., at various

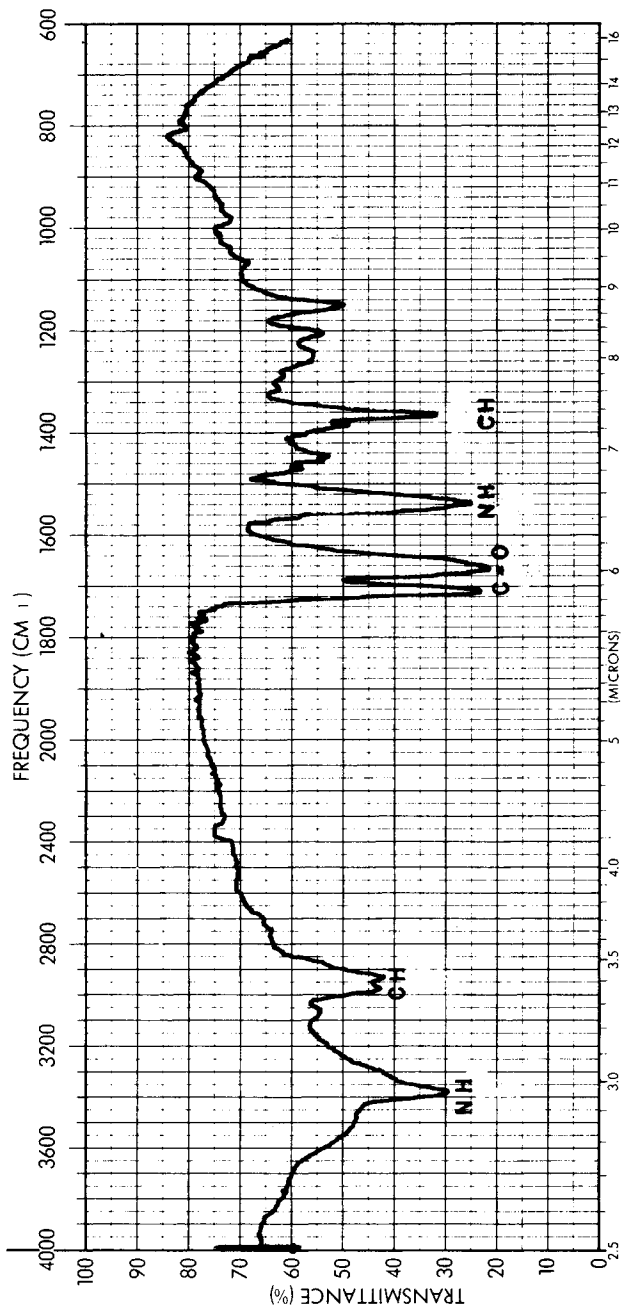


Fig. 5. Infrared spectra of PDAA deposited onto aluminum shots in the packed bed by electro-polymerization.

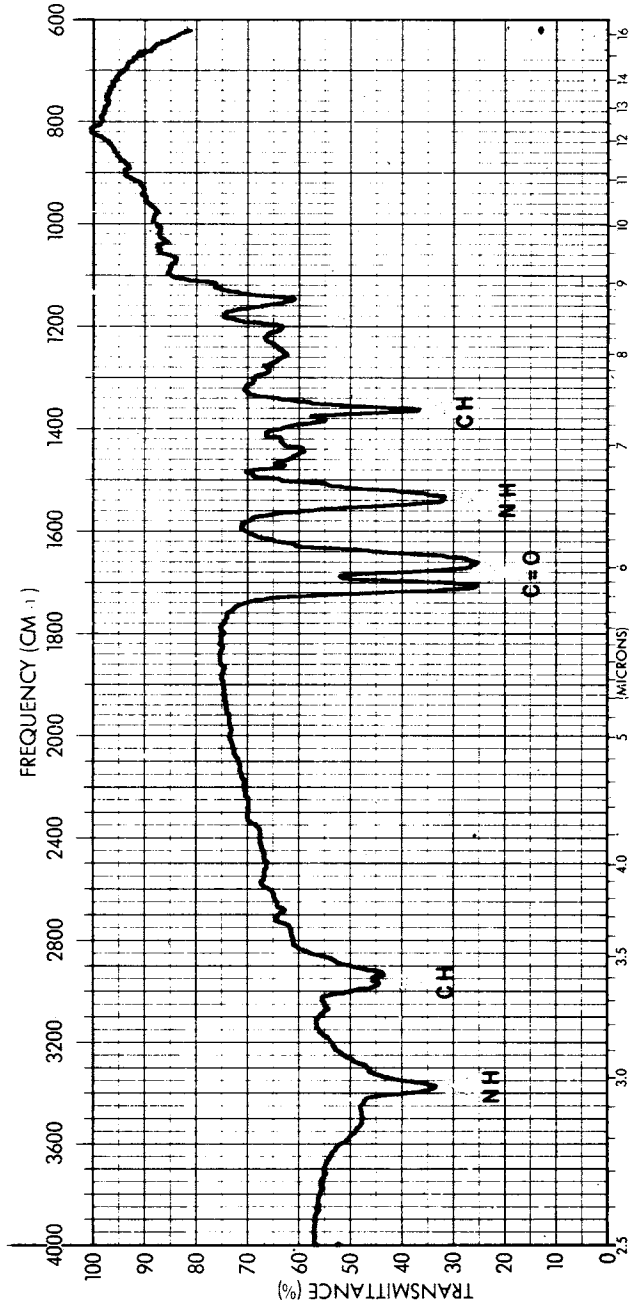


Fig. 6. Infrared spectra of PDAA deposited onto aluminum shots in the fluidized bed by electro-polymerization.

TABLE I
Composition of PDAA^a Coatings Deposited on Metal Electrodes

Metal	% N ^b	% C ^b	% H ^b	% Al ^c	% Fe ^c	% Cr ^c	% metal oxide ^d
Al	0.93	24.4	4.5	30.5	—	—	57.6
S-steel	12.0	33.4	4.9	—	13.3	3.9	30.0

^a 0.5M DAA monomer with 0.1N H₂SO₄ as electrolyte, flow system.

^b Composition obtained by elemental analysis.

^c Composition obtained by neutron activation analysis.

^d Oxide form of metals is assumed (M₂O₃).

degrees of bed expansion). It can be seen that higher flow velocities (higher degree of fluidization) give rise to higher current densities. This is similar to that in Figure 2 wherein the pseudo-current-density obtained for the fluidized bed case is higher than that for the packed bed (lower flow velocity). It should be realized that there is a considerable loss of surface area as a result of the packing of the bed and that this loss is regained on fluidization; and hence a higher degree of fluidization can utilize more of the available surface area and hence a higher pseudo-current-density. Also, it can be seen that for the case of the single aluminum cathode plate, the plane electrode current density which is based on the exposed surface area of the electrode itself increases as the flow velocity increases, as shown in Figure 4, in view of an increase in total current similar to that in the packed and fluidized bed cases.

After a polymerization time of 90 min, the white coating on the aluminum particles is dissolved in dimethyl formamide (DMF) solvent under room temperature over 24 hr; the dissolved polymer solution is transferred to the NaCl cell for drying for 24 hr, under 30°C. Infrared analyses are used to show the formation of the polymer film on the aluminum shots. For a sample of poly DAA, the peaks for N—H band are at 3380 cm⁻¹ (frequency) and 1540 cm⁻¹ and for C=O band at 1650 cm⁻¹ (Figs. 5 and 6). The elemental analyses (Table I) of the polymer film scraped off aluminum and stainless steel plates show the experimental values of nitrogen, carbon, and hydrogen compositions are somewhat different from the theoretical values which are 8.3%, 63.9%, and 8.8%. This difference is due to the presence of some metal oxide appearing with the coating and this is confirmed through neutron activation analysis. These results are also included in Table I. It is recognized that some metal surface due to the flow of the monomer-electrolyte system past the surface. Bonding does occur between this metal oxide and the polymer formed, especially in the case of the aluminum cathode,⁶ where the presence of the oxide layer is more pronounced. Thus, the metal oxide shown in Table I is not only the combined form but is also an artifact of the sampling and scraping techniques.

CONCLUSIONS

The work reported here clearly demonstrates the applicability of packed and fluidized bed systems in electroinitiated polymerization for development of polymeric coatings on metal surfaces. It is also shown that considerably higher total currents are possible in the case of the fluidized bed electrode and that the current density increases as the flow velocity increases for both the fluidized bed electrode and the plate electrode.

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