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FINAL REPORT

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ABSTRACT

Reported here is a summary of studies examining some problems in an energy conversion system. Regenerative fuel cell systems have been suggested for future manned space missions, but to meet the needed specific power requirements substantial improvements in the state-of-the-art technologies are needed. Similar improvements are needed, with emphasis on cost reduction in addition to higher conversion efficiency, for fuel cell systems that have potential for terrestrial applications. Polymer electrolyte membrane (PEM) fuel cells have been identified as promising candidates for development that would lead to the desired cost reduction and increased efficiency.

INTRODUCTION

This report is a summary of studies funded by the National Aeronautics and Space Administration which addresses some problems inherent in some energy conversion systems. The system of primary interest is one involving the conversion of solar radiation to forms useful to spacecraft and to planetary settlements. By use of regenerative fuel cells (which require reliable and efficient electrocatalysis), solar energy can be stored during dark periods. Regenerative fuel cell systems have been suggested for future manned space missions, but to meet the needed specific power requirements, substantial improvements in the state-of-the-art technologies are needed.

Fuel cell systems have a potential for terrestrial applications in addition to solar energy conversion in space applications. However, similar improvements are needed, with emphasis on cost reduction in addition to higher conversion efficiency. Polymer electrolyte membrane (PEM) fuel cells have been identified as promising candidates for development that would lead to the desired cost reduction and increased efficiency. Catalysts and electrodes for PEM fuel cell and electrolyzer systems are under development and evaluation. Small fuel cell stacks, for hydrogen and oxygen, and for hydrogen and air, are being tested and evaluated.

Another promising use for PEM fuel cells, particularly for terrestrial use, is the direct conversion of small, hydrogen-containing molecules, such as methanol, in the fuel cell, obviating the need for prior reforming to hydrogen.

RESULTS and DISCUSSION

In considering improvement(s) in the state-of-the-art technologies for required efficiencies, perhaps the most important consideration must be given to the membrane.

The present, generally available 'starting point' material is Nafion 117 (made by Dupont). This material is 7 mils (175 μm) thick, 1100 equivalent weight (EW) and conductivity of about 7.5×10^{-2} S cm^{-1}. Different thicknesses and equivalent weights of Nafion are available (e.g. 5,7,10, and 14 mil, and 950, 1100, 1200, and 1500 EW). The conductivity of 1100 EW Nafion is about $4.5\text{-}7.5 \times 10^{-2}$ S cm^{-1} (27-92° C), of 1200 EW about $3.1\text{-}5.0 \times 10^{-2}$ S cm^{-1}(37-92°C), and of 1500 EW, $2.2\text{-}3.3 \times 10^{-2}$ S cm^{-1} (41-92°C). In general, thicker membranes give lower electrical output than thinner membranes, and, also, in general, higher equivalent weight material gives lower electrical output than lower equivalent weight material. The fluorinated backbone of Nafion contains the same elements as a combination of the Teflons TFE, FEP, and PFA. The material is a relatively dilute acid, behaving as a typical aqueous acid from the viewpoint of conductivity and also limited in use to temperatures below the boiling point of water unless high water vapor pressures are used. Similar material, also perfluorinated proton exchange membrane material, is available from DOW Chemical Co. (equivalent weight 800, normally 125 μm thick) and from the Asahi Chemical Industry Co. (equivalent weight 1000, 125 μm).

These membranes, constituting the solid electrolyte in PEM fuel cells, are perfluorosulfonate ionomers consisting of flurocarbon main chains, with ionizable side groups which are usually a sulfonic acid. The fluorocarbon main chain is thermally and chemically stable; the sulfonate sites render these membranes cationically conductive. Only Nafion 117 is commercially available and is rather expensive. Therefore, alternative methods for preparing ionomers that are chemically similar to the perfluorosulfonate ionomers are being explored.(Ref. 1.) In one method, plasma polymerization was used to prepare ionomer films. Thin ionomer films can be plasma polymerized using TFCE and TFMSA. However, the ionic conductivities were substantially lower than Nafion 117. Alternative methods for plasma polymerization of ionomer films from these monomers were also explored. Procedures were developed that provide films with higher sulfonation levels, and higher conductivities, than originally obtained:

2.5×10^{-5} to 5×10^{-5} S cm^{-1}
4.3×10^{-5} to 6.1×10^{-5} S cm^{-1}
4.3×10^{-4} to 5.8×10^{-4} S cm^{-1}

The third film described is an order of magnitude more conductive than the other two. The explanation suggested is that the sulfonation level is significantly higher. It should be noted, though, that the conductivity is still less than Nafion.
These films were also plasma polymerized onto the surface of a microporous alumina filtration membrane to yield thin-film composite membranes. Plasma polymerized perfluorinated ultrathin polymer films containing sulfonic acid groups were obtained from a gaseous mixture of trifluoromethanesulfonic acid and hexafluoropropylene. (Ref. 2.) The applied RF power has a large influence on the decomposition of sulfonic acid groups; the degree of decomposition increased with decomposition of sulfonic acid groups; the degree of decomposition increased with RF power. Plasma polymer formed at RF power lower than 10W behaved as a cation-exchanger. The plasma polymerized thin film prepared at 5W was about 1 μm thick and free of pinholes. The film had a cross-linked structure and showed a higher cation permselectivity than Nafion 117 in aqueous KC1 system; however, the specific ionic conductivity was much lower than Nafion 117:

	t_K	Conductivity (S cm^{-1})	Capacity (meq g^{-1})
Plasma Polymer	0.99	1.8 x 10^{-4}	0.7
Nafion 117	0.97	7.5 x 10^{-2}	0.9

....in 0.5 M H_2SO_4

Further work is planned and the enhancement of ionic conductivity is expected by the suppression of the decomposition of sulfonic acid groups in the plasma and the enhancement of the ion exchange capacity.

Due to the fluorine chemistry needed for the production of the Nafions (and chemically similar materials) costs will remain high. A fluorine-free or partially fluorinated membrane could offer a substantial cost reduction potential for PEM technology. Partially fluorinated proton exchange membranes have been produced by radiation grafting for applications other than fuel cells at considerably lower cost. In one work (Ref. 3.), five different types of membranes were synthesized. The membranes are grafted copolymers of poly (tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) and sulfonated polystyrene, using divinylbenzene and triallyl cyanurate as cross-linkers. The resulting membranes contain only 30-40 % of the fluorine of Nafion 117 per unit area. It was noted that physical properties, such as water uptake and specific resistance, are strongly influenced by the nature of the cross-linker, (as well as fuel cell performance and stability of the membrane). The best performing membrane exhibited a lower resistance than the commercial Nafion 117 membrane, in a H_2 /O_2 fuel cell for up to 1000 h of continuous operation. This result demonstrates that the rate of disintegration under fuel cell conditions of hydrocarbon containing membranes can be significantly reduced by optimizing the membrane composition. It was speculated that future development of a fluorine-free membrane may not be an improbable vision.

Other alternative PEM membranes using simpler and less expensive chemistry than perfluorinated sulfonic acid polymers are being developed by several companies. Most of the work, though, is proprietary. Some of the work involves the synthesis of a series of sulfonated polyaromatic polymers and fabrication into membranes by solution casting. Results indicate that sulfonated polyaromatic membranes in various combinations of equivalent weight (EW range 375-920) and membrane thickness can perform equally or better than standard Nafion 117. Long term performance, though, has to be shown. Other work involves sulfonation of poly (arylene ether sulfones) and poly (aryl ether ketones) and subsequent crosslinking.

Another approach utilizes a reinforced composite made from PTFE and fluoroionomer. Samples have been provided in thicknesses of about 5, 10, and 20 μm, and EW ionomeric components of 900 or 1100. Membrane conductances of about 80 S cm $^{-2}$ for a 12 μm thick membrane at 25 °C have been reported. (Nafion conductance is about 5-7 S cm $^{-2}$ under similar conditions). Membranes have also been obtained from sulfonation of commercially available styrene-ethylene/butylene-styrene triblock polymer. These membranes will be tested for use in PEM fuel cells. They were developed seeking to mimic the Nafion structure with inexpensive hydrocarbon-based block copolymers.

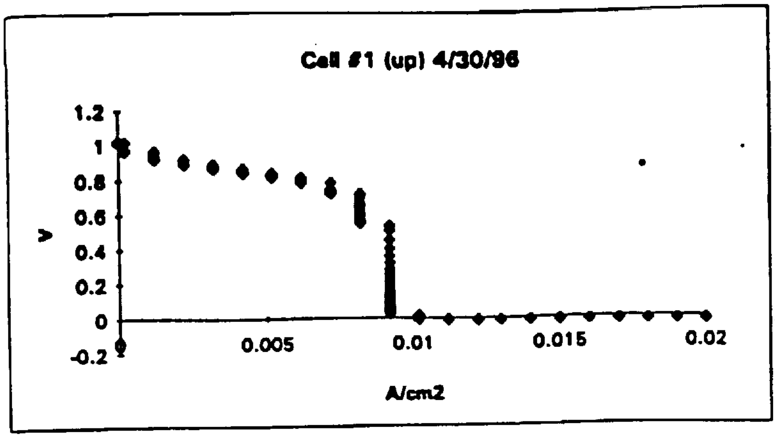
In considering the direct conversion of small, hydrogen-containing molecules in the fuel cell, methanol has been the most studied. As with $H_2/0_2$ in PEM systems, the 'starting point' material for the electrolyte was Nafion 117 for use in cells at 60-100 °C. A major problem in present direct methanol fuel cell technology is the amount of methanol crossover through the membrane. In examining various Nafions it was found that higher equivalent weight, 1500 EW, e.g., has lower crossover than 1100 EW material. And that thicker, 14 mil 1100 EW, has lower crossover than thinner, 5 mil 1100, material. One approach to reduce crossover and yet retain acceptable conductivity and performance is to use a laminated membrane, e.g., a 1 mil 1500/5 mil 1100 composite. Other Nafion-like composites are being developed and tested, and attempts are being made to modify both the surface and the bulk to reduce crossover. Enhanced cross linking is also being tried. Other attempts at composites have involved cross-linked polystyrene sulfonic acid and polyvinylidene fluoride. Results have shown a composite membrane similar to Nafion 117 in conductivity, but with a methanol crossover one-tenth that of Nafion 117.

It is generally conceded that at present the requirements for large-scale transportation or stationary power generation applications have not yet been met. No fuel cell stack meeting those requirements is now available. In considering cost reduction and higher conversion efficiency, several approaches are being investigated. Some of the problems with PEM fuel cells are related to the temperature of operation. With PEM cells, electrolytes tend to dry at temperatures > 73 °C, and the voltage decreases. It is common practice to use humidification systems to avoid humidification problems. However, this is one of the areas where simplification and cost reduction can be achieved if this need can be obviated. Thus there is work on improving MEAs and finding some that are less susceptible to imperfections in humidification and water removal and also that have improved performance at close-to-atmospheric pressure. Studies have shown that for low power level systems the use of pressurized air should be avoided in order to reduce both the parasitic power losses for compression as well as system complexity. This however requires further improvement of the materials in order to operate the stacks at near atmospheric pressure levels. Pressurized operation has been important because it affords better gas distribution and membrane humidification. At lower temperatures water tends to condense and flooding problems occur in the cells. One method to overcome this problem is to remove condensed water by capillary force using some hydrophilic materials. Another approach is to prevent water vapor from condensing by adjusting the cell temperature(s), specifically the temperature difference between the gas inlet and outlet in the cell. In general, it seems that if PEM cells are operated between 67-77 ° C, water requirements and water removal can be controlled appropriately.

Experimental

Beginning measurements were made using a 7-cell, 50 cm^2 , stack with Nafion 105 obtained from ElectroChem, Inc., Woburn, MA. The reactant gases were H_2 and 0_2. They were not humidified or heated. The stack was run at atmospheric pressure and room temperature.

The data shown is one set showing a performance curve, from open circuit to very low voltage, and then a return to open circuit. The stack was instrumented to measure individual cells, so that the behavior of each could be observed. From the observed behavior a determination can be made of initial structural 'defects', later temporary or permanent defects developed during endurance testing.



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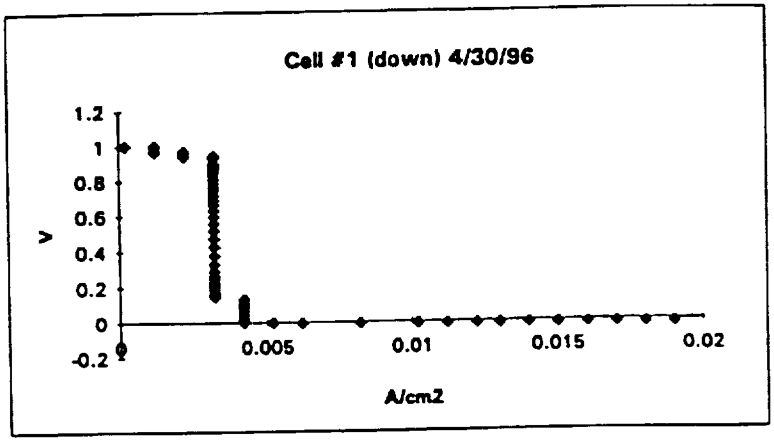

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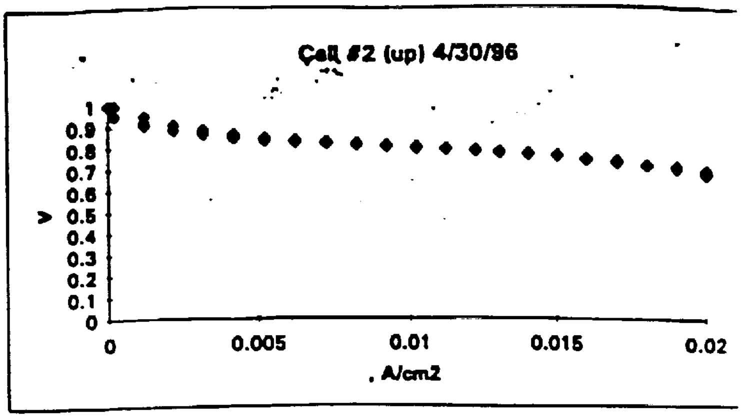

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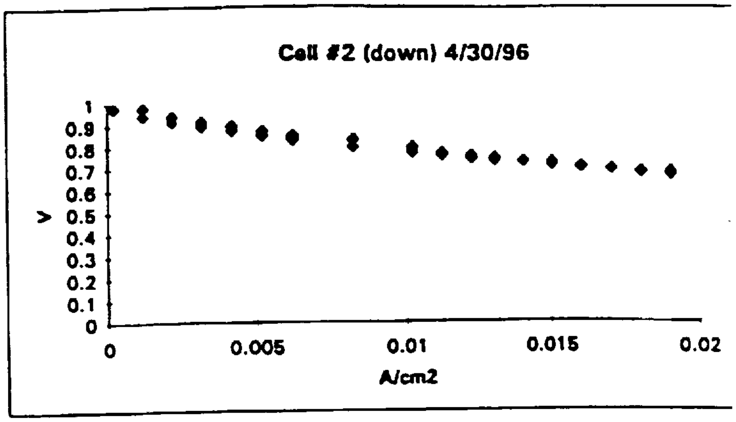

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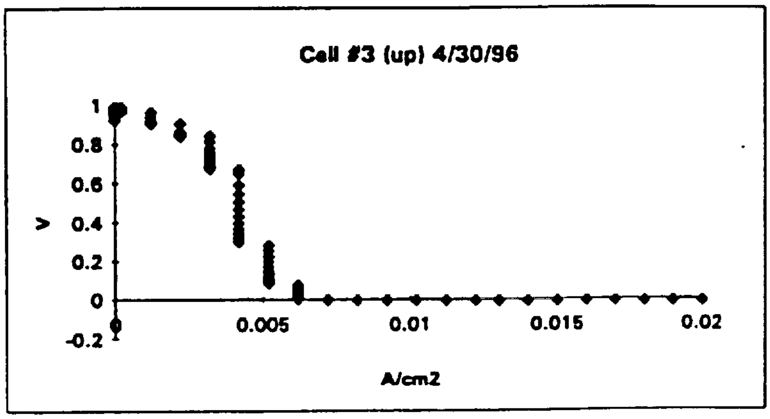

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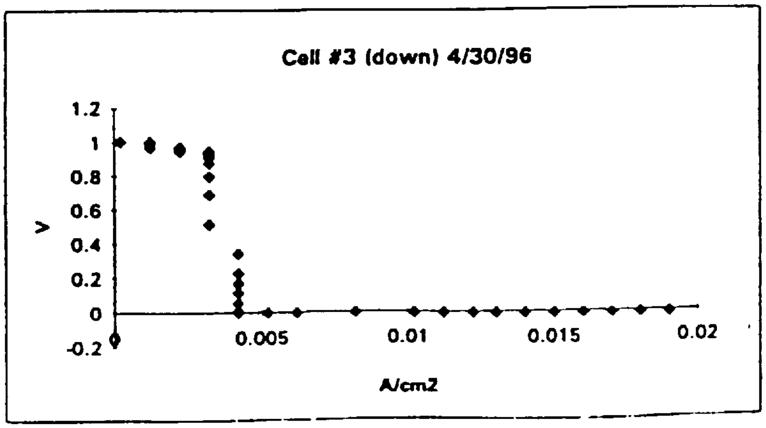

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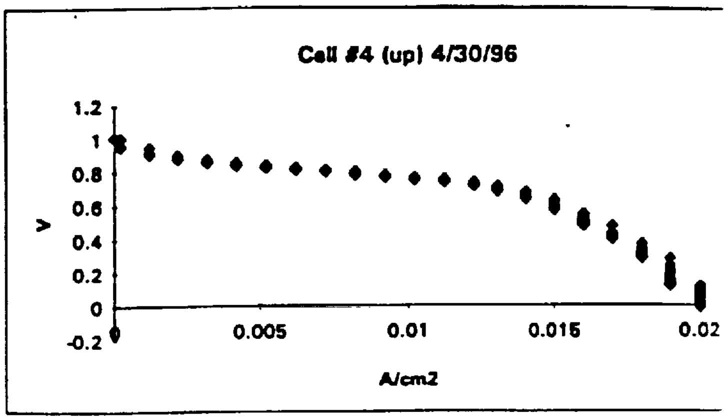

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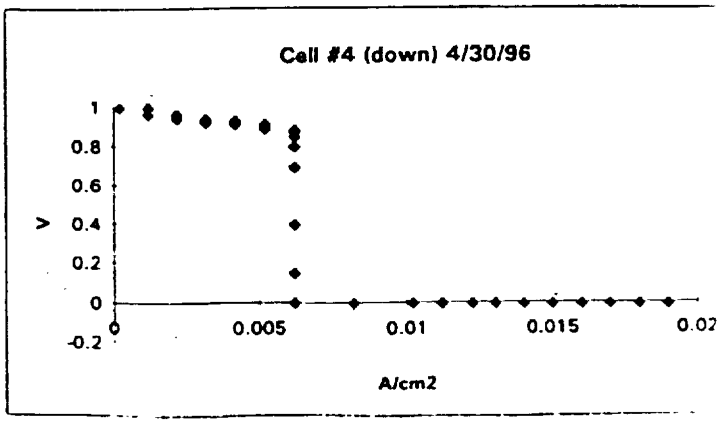

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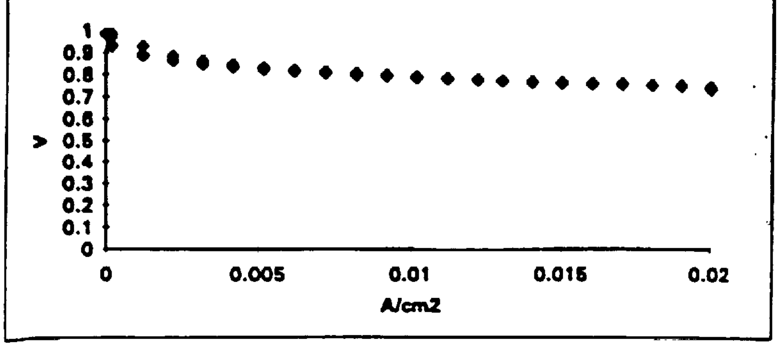
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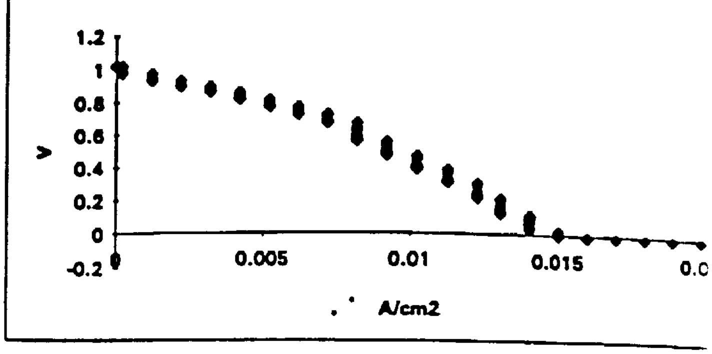
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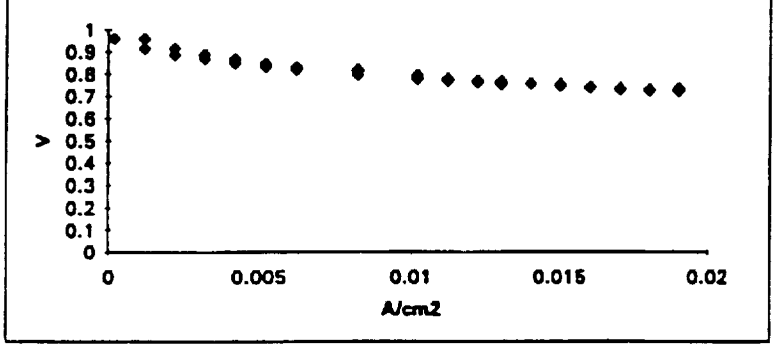
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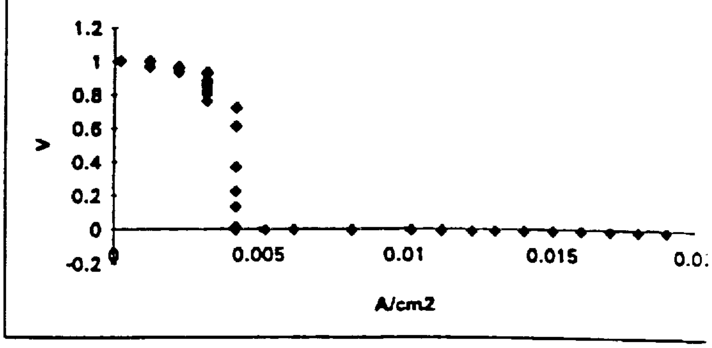
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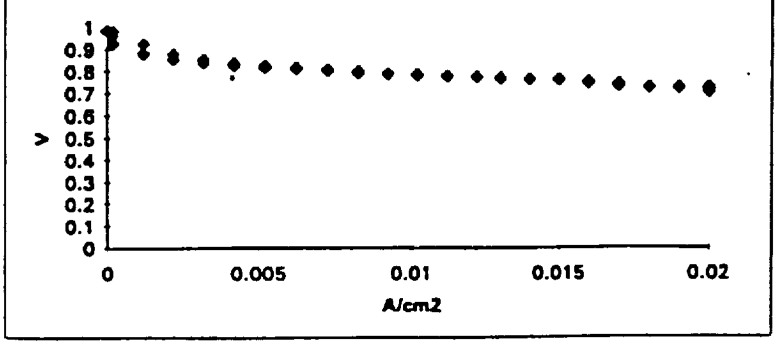
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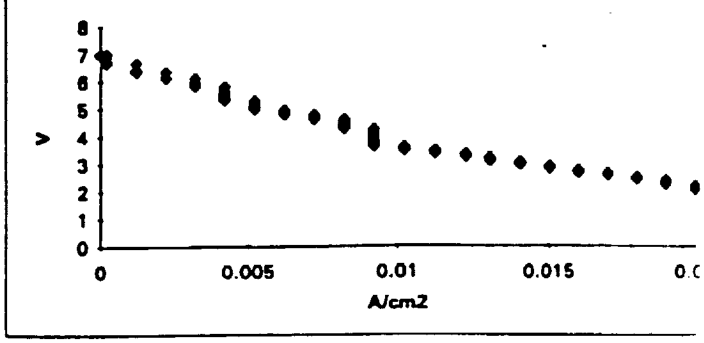
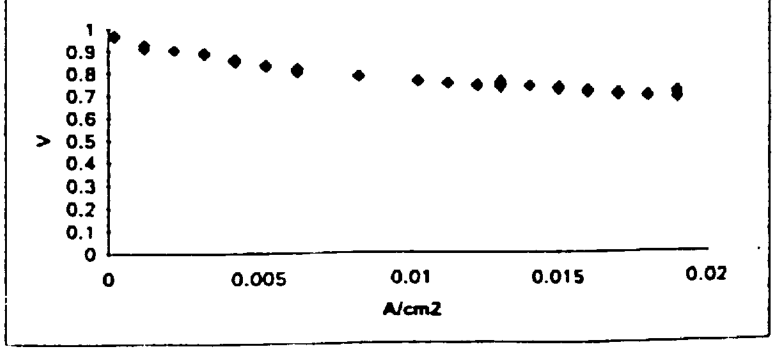

Stack (up) 4/30/96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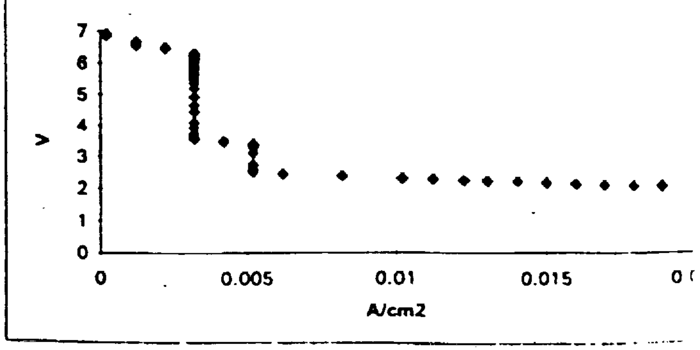
Stack (down) 4/30/96

References

1. C.J. Brumlik, A. Parthasarathy, W-J. Chen, and C.R. Martin, J. Electrochem. Soc., **141**, 2273 (1994).

2. K.Yasuda, Y. Uchimoto, Z. Ogumi, and Z. Takehara, J. Electrochem. Soc., **141**, 2350 (1994).

3. F.N. Büchi, B. Gupta, O. Haas, and G.G. Scherer, J. Electrochem. Soc.,**142**, 3044 (1995).