Composite fiber structures for catalysts and electrodes

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Abstract

We have recently envisioned a process wherein fibers of various metals in the 0.5 to 15 μm diameter range are slurried in concert with cellulose fibers and various other materials in the form of particulates and/or fibers. The resulting slurry is cast via a wet-lay process into a sheet and dried to produce a free-standing sheet of 'composite paper'. When the 'preform' sheet is sintered in hydrogen, the bulk of the cellulose is removed with the secondary fibers and/or particulates being entrapped by the sinter-locked network provided by the metal fibers. The resulting material is unique in that it allows the intimate contacting and combination of heretofore mutually exclusive materials and properties. Moreover, due to the ease of paper manufacture and processing, the resulting materials are relatively inexpensive and can be fabricated into a wide range of three-dimensional structures. Also, because cellulose is both a binder and a pore-former, structures combining high levels of active surface area and high void volume (i.e., low pressure drop) can be prepared as free-standing flow through monoliths.

Introduction

Electrode structures and catalysts which function at a steady-state conversion level must simultaneously accommodate a number of physical processes including, among others: surface and interface kinetics and selectivity, heat transport, mass transport, thermal and/or electrical conduction, corrosion and sintering/deactivation. To beneficially accomplish these physical processes electrode/catalyst designers must consider a number of individual design factors including void volume, specific surface areas of both catalytic/electrocatalytic materials and supports, micro- and macroporosity, mechanical stability, cost, safety and the addition of various additives and binders to promote wettability, hydrophobicity, reactant contacting and interfacial mass transport.

Many of the high surface area electrodes in use today are fabricated from particulate-based materials which are retained onto a screen/collector by means of various organic and polymeric binders (e.g., PTFE). Due to the packing constraints provided by these particulates and binders, free-standing electrode structures are only available in a limited range of flexibilities, void volumes and macroporosities. The resulting effectiveness factors and Thiele moduli often preclude the effective utilization of high surface area catalysts/electrocatalysts because of intra-electrode heat and mass-transport limitations.

The focus of this effort is to utilize fibrous precursors as building blocks for enhanced electrode and catalyst structures. There are a number of inherent advantages in using these materials in electrically conductive and/or high surface area structures. Furthermore, the high aspect ratio possessed by fibers allows fabrication of free-standing structures of higher void volume and less resistance to both heat and mass

transport. The process described herein also utilizes the sinter-attachment of micronic metal fibers to provide necessary mechanical contacting and stability. This feature eliminates the *a priori* use of void-filling binders unless they are critically required for other chemical reasons.

Experimental

Details of paper preform fabrication, sintering conditions, optimization considerations, choice of materials and other electrode preparation techniques may be found in refs. 1 to 7.

Fabrication of monolithic structures

Due to the ease of paper processing and handling, preform sheets may be corrugated and rolled or layered so as to create flow channels for low transport resistance and high accessibility of the constituents (Fig. 1). Preform sheets may also be layered prior to sintering so as to create thicker electrodes/catalysts which can readily accommodate graded porosities and graded compositions depending upon the number and type of sheets which are stacked. Preform sheets incorporating ceramic fibers and cellulose may also be layered into a stack so as to integrally incorporate an electrolyte separator.
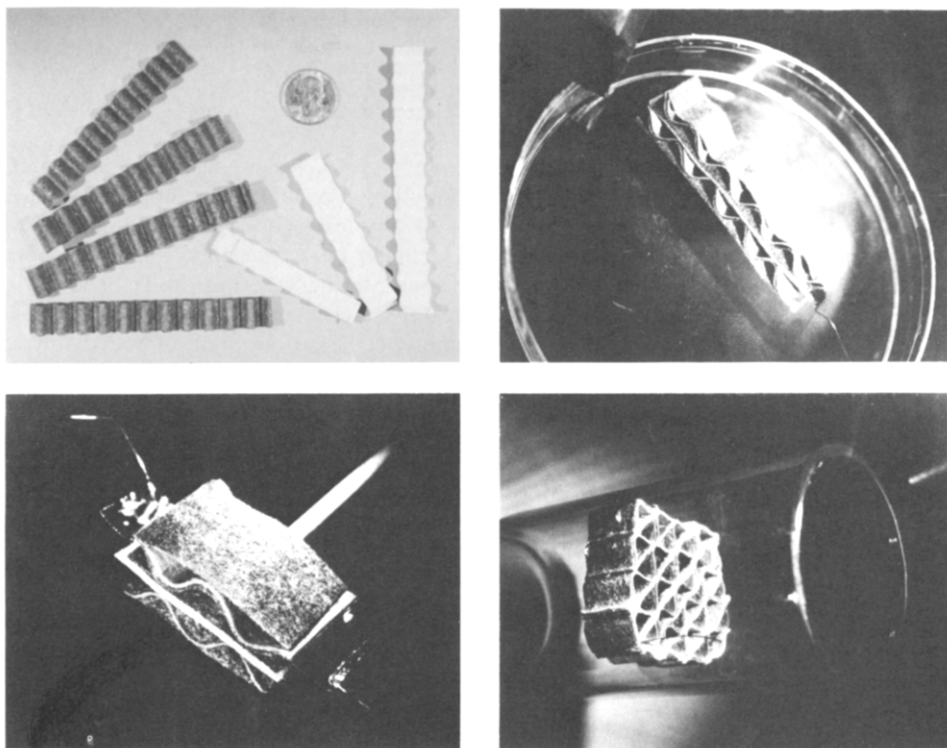

Fig. 1. Fabrication of electrode and catalyst monoliths.

Metallic fibers in the preform permit these materials to be sintered into various current collectors and metallic surfaces. Cyclic voltammetry and other electrochemical techniques generally demonstrate excellent mechanical and electrical connectivity between micronic metal fibers, high surface area activated carbon fibers and the various substrates depicted. The only exception being the interior of a tube. Upon sintering and cellulose removal, there is a net shrinkage of the preform causing it to adhere quite tightly to the exterior of a curved surface, whereas there is a net recession away from the interior surface. This problem has been addressed by presintering to a metallic mesh followed by attachment to the interior. The geometries appear to meet many of the requirements necessary for incorporating fibrous materials into real devices while permitting electrical conduction as well as appropriate heat and mass transport.

Inclusion of ceramics, refractories and catalysts: concomitant impact on void volume

When high surface area and electrically conductive electrodes/catalysts are desired it is possible to incorporate activated carbon fibers from a variety of sources into the preform along with appropriate metal fibers. Activated carbon fibers provide free-standing structures with up to 98% void volume. Such void volumes are beneficial for promoting mass transport, however, volumetric reactivity and energy density are often sacrificed. This is especially the case for an electrochemical structure, where the void
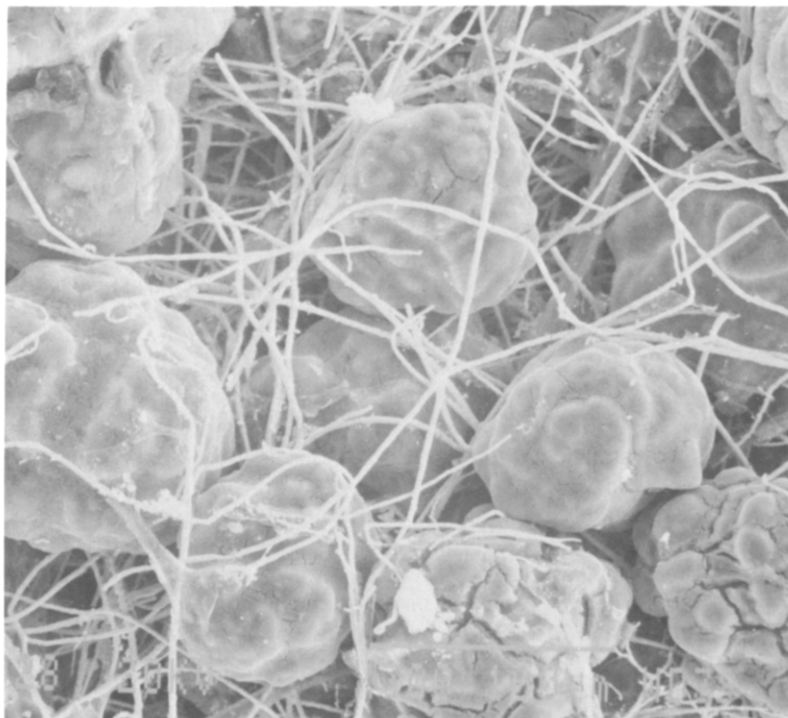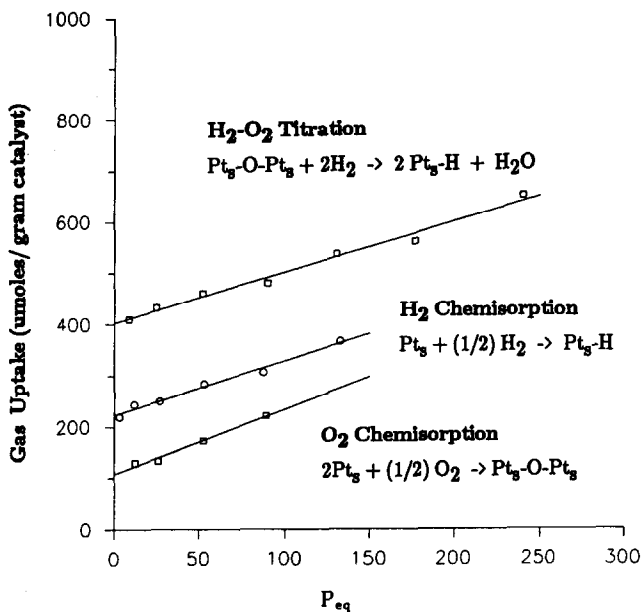

Fig. 2. Fibrous catalyst/electrode incorporating carbonaceous particulate; 6 g particulate:1 g steel fiber.

Fig. 3. Chemisorption and titration electrodes impregnated with platinum after sintering.

Catalyst	Impregnation method	Metal precursor	H_2 uptake (μmol)	Dispersion	Particle size (nm)
13.6% Pt/C	Soaking/ blotting	$(NH_3)_4Pt(NO_3)_2$	225	0.65	1.7

volume must be filled with the mass of a relatively low conductivity electrolyte. In these instances, the electrode/catalyst designer often requires a lower void structure and it is beneficial to use particulate-based materials along with metallic fibers. Particulates allow more dense packing and are available in a broad selection of physical properties at reduced costs compared with fibers.

To address the above-noted design consideration, Fig. 2 illustrates the feasibility of retaining catalytic/electrocatalytic particulates at various loading and compaction levels, approaching ~20% void volume. The high aspect ratio of the metallic fibers permits them to provide a 'binding' function at a fraction of the corresponding weight or volume required for an organic or particulate binder. Metallic fibers also impart superior electrical and thermal conduction. Moreover, intra-electrode potential drops and ohmic losses are minimized and there is an opportunity to use electrocatalytic materials and supports often considered too resistive for practical cell designs. As demonstrated in Fig. 2, loadings as high as 6:1, particulate:metal fiber, are readily obtained. Compaction and void volume are controlled by mechanical pressure before, after or during sintering, as well as the amount of cellulose added to the preform. The aspect ratio and geometry of the fibers and particulates also impact upon the void volume.
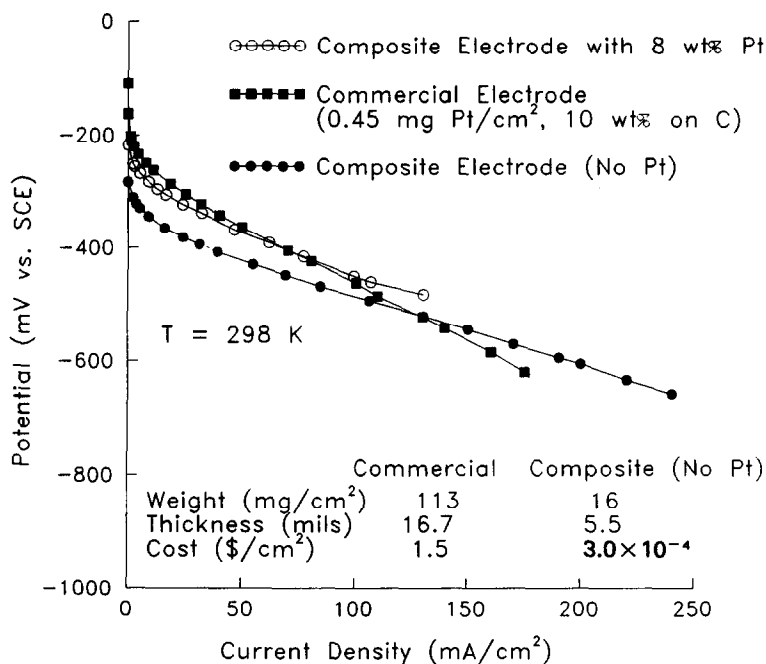
Fig. 4. Oxygen reduction in KOH half-cells.

Addition of precious metals

Figure 3 provides selective chemisorption data and O_2–H_2 titration data for a stainless steel-activated carbon fiber electrocatalyst following addition of platinum. Impregnation is via an incipient-wetness technique with the liquid exterior to the carbon fibers removed by wicking into an appropriate blotter. High dispersions are obtained provided the platinum is added after metal fiber sintering. Noncorrosive impregnation solutions must also be used to avoid attack on the stainless-steel fibers.

Transport resistance versus catalytic activity

Figure 4 provides polarization curves for oxygen reduction in a KOH half-cell, details of which are described elsewhere [8]. The salient feature of this plot is that a stainless steel–carbon fiber composite electrode (without platinum) can outperform a platinum-containing commercial electrocatalyst at higher current densities. Since the slopes of the polarization curves shown in Fig. 4 are proportional to the lumped resistance, it appears that the nascent reactivity and easy accessibility of the activated carbon in the composite fiber electrode permit it to operate with a reduced mass-transport limitation. Further details of this study and an impedance analysis of the various resistance terms are described elsewhere [8].

Conclusions

Mixed fibrous materials can be prepared from dissimilar materials to achieve physical properties which are often considered to be mutually exclusive using other

means or materials. The enabling attribute/requirement is the entrapment of one or more components within the sinter-bonded matrix of the other component. Unique variations of specific surface area, void volume, macroporosity, etc., are obtained. Particulate materials may also be incorporated into these structures as well as active electrocatalysts. The ease of paper-making and paper processing/reprocessing permits ready fabrication of various monoliths and integrated structures at relatively low cost.

The nature of this fabrication approach, and the physical attributes of the resulting materials, permit the electrode/catalyst designer to accommodate heat transfer, mass transfer, ohmic losses, interfacial kinetics and interphase contacting in a manner not previously available.

Acknowledgements

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