ADVANCED

MATTERNALS

1

2

$$R^2 = \frac{1}{n}$$
 $R^2 = \frac{1}{n}$
 $R^2 = \frac{1}{n}$
 $R^2 = \frac{1}{n}$
 $R^2 = \frac{1}{n}$
 $R^2 = \frac{1}{n}$

als. Polymer 2 may be cetylene (PA) and, in

monomer 3 in a controlled manner to a set of oligomers 4, which, after end capping and fragmentation reactions, were converted to separable polyenes 5, with seven to fifteen double bonds. [6] Finally, a variety of substituted 7-oxanorbornenes 6 were shown to polymerize to high molecular weight compounds in the presence of [W(OCH₂/Bu)₂(CH/Bu)Br₂], a similar tungsten catalyst. The importance of the nature of the catalyst was proven by subsequent addition of more electrophilic catalysts to polymer 7, when complete cleavage of 1,4-epoxy units was observed. [7] These monomers may also be polymerized by ruthenium based initiators like "RuCl₃·3H₂O" in the presence of water. [8]

The ROMP products 2, 5 and 7 have entirely novel structures and are inaccessible by other methods. These polymers are not only interesting from the view-point of basic research but show remarkable properties as materi-

als. Polymer 2 may be considered as precursor for polyacetylene (PA) and, in fact, was rearranged to PA the importance of which as a material is evident. Separated oligomers 5 are of interest in many respects, e.g. those concerning excited states in polyenes or their non-linear optical properties. Polymer 7 may act as an acyclic ionophore or as an ion permeable membrane. Thus, the new generation of ROMP catalysts has opened the way to a whole variety of novel polymers more of which might eventually gain industrial importance.

Arnulf-Dieter Schlüter

Max-Planck-Institut für Polymerforschung

Mainz (FRG)

Book Reviews

Carbon Materials

Carbon—Electrochemical and Physicochemical Properties. By K. Kinoshita. Wiley, New York 1988. xiii, 533 pp., bound, £ 65.00.—ISBN 0-471-84802-6

Carbon materials have been used in electrochemistry for several decades, both in laboratory apparatus and in industrial plants. In many of the applications there is no competition whatever from other materials. The large potential range, wide variety of morphology, good corrosion resistance, high electrical and thermal conductivity and

reasonable costs all contribute to carbon's benefit in electrochemical systems. Moreover, new types of materials such as pyrolytic graphite, glassy carbon and carbon fibers, have further extended the range of applications. However, many users today are not fully aware of the wide variety of carbons that can be produced by different manufacturing processes and—most importantly—neither do they know the individual physical and chemical properties of these forms. This lack of knowledge makes it difficult to

^[1] K. J. Ivin: Olefin Metathesis, Academic Press, London 1983.

^[2] R. L. Gilliom, R. H. Grubbs, J. Am. Chem. Soc. 108 (1986) 733.

^[3] J. Kress, A. Aguero, J. A. Osborn, J. Mol. Catal. 36 (1986) 1.

^[4] C. J. Schaverien, J. C. Dewan, R. R. Schrock, J. Am. Chem. Soc. 108 (1986) 2771.

^[5] T. M. Swager, D. A. Dougherty, R. H. Grubbs, J. Am. Chem. Soc. 110 (1988) 2973.

^[6] K. Knoll, S. A. Krouse, R. R. Schrock, J. Am. Chem. Soc. 110 (1988)

^[7] B. M. Novak, R. H. Grubbs, J. Am. Chem. Soc. 110 (1988) 960.

^[8] R. H. Grubbs, paper presented at the 3rd North American Chemical Congress, Toronto, June 1988.

ADVANCED

select the most appropriate form of carbon for any specific purpose. It seems that the main concern of the author K. Kinoshita is to bridge the gaps which exist in understanding the relevance of physicochemical properties to electrochemical specifications.

The book starts with a brief description of the manufacturing processes for carbon blacks, active carbons, graphite, glassy carbon and carbon fibers. Special emphasis is given to the commercial carbon blacks, i.e. channel blacks, oil-furnace blacks and thermal blacks.

The emphasis on carbon blacks continues in Chapter 2, which describes physical properties. Here the reader finds a thorough evaluation of the literature concerning crystallographic structure, surface area and porosity, morphology, heat treatment and electrical properties. The discussion in Chapter 3 focuses on the analysis of surface groups (chemical, spectroscopic and thermal analysis) and provides the basis for a better understanding of chemical reactivity, wettability and catalysis, the relevant properties for applications in electrochemistry. K. Kinoshita has succeeded in providing an excellent reference source on the physical, chemical and surface properties of carbons, most particularly carbon blacks. The description reflects the present state of knowledge, and will be of great use, not only to the electrochemist. It would have been desirable to use SI units consistently throughout the text. Data on the coefficient of thermal expansion, thermal conductivity and electrical resistivity in anisotropic graphite need to be corrected (pages 12 and 23).

Chapters 4 and 5 describe the chemical reactions as well as the characteristics and properties of carbon electrodes, thus helping the user to select specific carbon materials. In the section "nonporous structures" all the forms used in electrochemical studies are treated systematically, whereas in the section "porous structures" a distinction is made between flooded electrodes and gas-diffusion electrodes. Here again carbon black is shown to be a leading material and catalyst carrier, thus justifying the special emphasis accorded to it in the introductory chapters.

The author's approach of describing the electrochemical behavior of carbon separately (Chapter 6), rather than together with the individual applications proves to be advantageous. It allows the general aspects of electrochemical oxidation and electrocatalysis to be shown very clearly. The electrochemical reactivity of coal is also dealt with in Chapter 6.

After the efficient preparation in the preceding six chapters, the discussion devoted to the actual use of carbons in electrochemical systems is relatively short (Chapter 7, 80 pages). The reader may miss MnO₂ electrolysis as well as molten salt electrolysis yielding alkali metals and aluminum—the very applications that use by far the largest portion of carbon products. In addition, the application of carbon and graphite in chlor-alkali cells, including trials aimed at the introduction of an air-consuming cathode, appears to be treated too briefly. On the other hand the use

of carbon in fuel cells, especially phosphoric acid fuel cells, and also in batteries is treated thoroughly. Within this section special attention is again devoted to carbon blacks. Reference is made to the extensive efforts undertaken to increase the life of carbon black electrodes by heat-treatment, and also by preventing the material from reaching critical potentials where corrosion occurs. It is made apparent to the reader that considerable efforts are still needed to clarify the dependence of electrochemical behavior on physical and chemical properties.

The patent literature is not considered in the text. Instead a list of recent patents concerning fuel cells, bipolar electrode separators and batteries dated after 1980 is given in the Appendix.

The motivation for writing this book arose at a workshop held in 1983 where experts from materials science and the electrochemistry of carbon came together. The author's intention has clearly been to provide a reference source for researchers and technologists interested in the electrochemistry and the electrochemical applications of carbon materials. This aim has been fully achieved. Skilful subject division, a thorough evaluation of the relevant literature and properly arranged tables all combine to make *Kinoshita*'s book an easily readable work of reference which can be highly recommended.

Graphite Fluorides. By N. Watanabe, T. Nakajima and H. Touhara. Elsevier, Amsterdam 1988. xi, 263 pp., bound, DFl 220.00.—ISBN 0-444-42885-2

The preparation and study of graphite fluorides goes back to the work of O. Ruff, O. Bretschneider and F. Evert (1934) and that of W. Rüdorff and G. Rüdorff (1947). The senior author of the book reviewed here, N. Watanabe, became interested in these graphite compounds while studying the "anode effect". It is undoubtedly this fact which has persuaded him to devote the first chapter of his book to the anode effect, which occurs at carbon anodes when they are used in molten fluoride electrolysis. N. Watanabe and his research group have worked continuously since 1961 on elucidating the chemistry of the graphite fluorides. He and his co-authors are ideally qualified to give a comprehensive account of the field.

Chapters 2 to 4 deal respectively with the preparation, the structure, and the surface properties and chemical properties of graphite fluorides. The experimental observations are described in detail with the help of numerous diagrams and tables. The interpretation of thermogravimetric data and of the X-ray, IR, NMR and X-ray photoelectron spectra is reported at considerable length, based mainly on the authors' own results. It has not been possible to avoid some repetition within the book; however this enhances its usefulness as a work of reference.

A considerable proportion of the book (about 100 pages) deals with technological applications. The outstanding properties of low surface energy, low bonding energy be-