Electrochemical Carbon

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Contents

I. Introduction

A. Scope and Definition of Terms

With respect to general terminological conventions,[1] the name *electrochemical carbon*[2] denotes "synthetic solids consisting mainly of atoms of the element carbon", which can be prepared electrochemically from suitable precursors. (For the definition of "electrochemical carbonization", see section I.B). Of the precursors, we shall skip carbon-like materials; hence, electrochemical reactions of elemental carbon, such as intercalation, surface modification, etc.,[3-6] will not be considered. For the same reason, we have to skip also electrochemical synthesis of carbon nanotubes and onions discovered recently by Kroto et al.[7-10]

Electrochemical preparation of elemental carbon from its compounds is, in principle, possible either by anodic oxidation (e.g., of hydrocarbons) or cathodic reduction (e.g., of carbon oxides or halides). Model reactions:

$$CY - e^- \rightarrow C + Y^+ \tag{1a}$$

$$CY + e^- \rightarrow C + Y^- \tag{1b}$$

(Y denotes general substituent(s)) may be thermodynamically very favored. For instance, the standard redox potentials CY/C (for selected precursors in parentheses) equal[2] the following: 1.19 (CCl_4), 0.56 (CF_4), 0.52 (CO), 0.21 (CO_2), 0.13 (CH_4), and −1.08 V (C_2H_2). However, the redox carbonizations are often slow and complicated by side reactions. Many important processes are based on reductive carbonizations, in which typical precursors are perhalogenated hydrocarbons.[2,11] Table 1 surveys some examples of electrochemical carbonization processes[2,11-47] which will be further discussed in detail below. This paper updates a previous review of electrochemical carbonization of fluoropolymers,[2] while a special attention is paid to other carbon precursors, and papers published during 1991 to mid-1997.

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Table 1. Selected Examples of Electrochemical Carbonization Processes[a]

precursor	working electrode	potential (V)	reference electrode	electrolyte (solution)	product/notes	refs
			Anodic Processes			
H−C≡C−H	Pt	1.5	SCE	$LiClO_4$+ DMF	carbyne-like	12
pyridine, ...	Ag	0.12−0.45	SCE	KCl (KF) + H_2O	photoelectrochemical (SERS)	13, 14
			Cathodic Processes			
CO_2/CO_3^{2-}	Pt, Au, Ag, Ni	−1	Ag/Ag^+	carbonate eutectic,700 °C	C/EC mechanism	15, 16
CO_2	Cu	−1.6	SCE	$KHCO_3 + H_2O$	graphitic/poisoning of Cu	17−19
PTFE	C-composite	1	Li/Li^+	$LiClO_4$ + THF + DME	C/Li battery application	20
PTFE	C-composite	1.4	Li/Li^+	$LiPF_6$ + EC + DEC	C/Li battery application	21
PTFE	Pt	−2	SCE	NBu_4BF_4 + DMF	graphitic/intercalated NBu_4^+	22−26
PTFE	GC, Fe	−2.6	SCE	NBu_4ClO_4 + DMF	carbyne-like	27−30
PCTFE	C-composite	1.5	Li/Li^+	$LiBF_4$ + γ-butyrolactone	carbyne-like	31, 32
PVDF	Pt	galvanost		NBu_4ClO_4 + DMF	carbyne-like	33
I−C≡C−I	Pt	−2	SCE	NBu_4I + DMF	carbyne-like	34, 35
HCBD	Pt	−2	SCE	NBu_4ClO_4 + DMF	carbyne-like	36, 37
HCBD	Pt, GC	−3	Ag/Ag^+	NBu_4BF_4 + AN	graphite/reverse dopable	38−41
CCl_4	Pt, Ni, Cu, ...	galvanost		NBu_4BF_4 + AN	carbonaceous fibers	42
fluorographite	C-composite	1.5	Li/Li^+	$LiClO_4$ + PC	graphite/Li battery	43
			Amalgam/Cathodic Processes			
PTFE	C-as grown	0.91[b]	Li/Li^+	C−MF (solid electrolyte)	carbyne-like	44, 45
C_xF_{2x+2}[c]	C-as grown	0.91[b]	Li/Li^+	C−MF (solid electrolyte)	carbyne-like	44, 45
PCTFE	C-as grown	0.91[b]	Li/Li^+	C−MF (solid electrolyte)	carbyne-like	44, 45
Nafion 117	C-as grown	0.91[b]	Li/Li^+	C−MF (solid electrolyte)	carbon modified by $-SO_3^-$	46
C_6F_6	C-as grown	0.91[b]	Li/Li^+	C−MF (solid electrolyte)	graphite-like	45, 47

[a] AN, acetonitrile; Bu, butyl; DEC, diethylene carbonate; DME, dimethoxyethane; DMF, dimethylformamide; EC, ethylene carbonate; GC, glass-like carbon; HCBD, hexachlorobuta-1,3 diene; PC, propylene carbonate; PCTFE, poly(chlorotrifluoroethylene); PTFE, poly(tetrafluoroethylene); PVDF, polyvinylidene fluoride; SCE, saturated calomel electrode; THF, tetrahydrofuran. [b] Thermodynamic value for Li-amalgam.[2] [c] x = 2,6,9,20,24.

B. General Features of Electrochemical Carbonization

The CY bond breaking, promoted by electron transfer (for a review, see ref 48) already proceeds at low (room) temperatures. It is an alternative process to pyrolytic reactions, common in carbon chemistry. Consequently, the structure and properties of an electrochemical carbon may differ considerably from those of the usual pyrolytic carbons. For instance, electrochemical carbons often show a very peculiar carbyne-like structure (Table 1) which is based on linear sp-bonded carbon chains (for a brief review, see ref 11 and section VI.B).

Electrons in reactions 1a and 1b are supplied either through redox-active molecules (chemical carbonization) or through an electrode, which contacts an ionically conducting solid or liquid phase and the precursor (electrochemical carbonization). A sharp distinction between "chemical" and "electrochemical" processes cannot be drawn. First, the carbonization might proceed via electrochemical generation of reactants, which subsequently convert CY to elemental carbon chemically (EC mechanism). Second, some reactions of CY, normally regarded as chemical processes, are, in fact, electrochemical ones. This was first clearly demonstrated by the reduction of poly(tetrafluoroethylene) (PTFE) with liquid alkali metal amalgams (M(Hg)).[49−52]

1. Electrochemical Carbonization with Amalgams of Alkali Metals. Jansta and Dousek[49−52] have found that the processes occurring at a "dry" interface of an alkali metal amalgam and PTFE are inherently electrochemical reactions in a short-circuited galvanic cell. The reaction PTFE/M(Hg) yields a fully defluorinated polymeric carbon in a mixture with a stoichiometric amount of alkali metal fluoride (MF, MF/C = 2). There are two main arguments against "chemical" interaction of PTFE with M(Hg) (except for the initialization stage): (i) The reduction rate is almost independent of the amalgam concentration (between ca. 1 and 10^{-5} at%).[52,53] (ii) The product mixture (C−MF) is free from mercury (<0.2 wt % Hg).[54] Since C−MF is impermeable to the amalgam, it separates perfectly both reactants after the formation of the first monolayers of the product. Nevertheless, the reaction PTFE/M(Hg) proceeds smoothly and quantitatively until one of the reactants is consumed.[51,52]

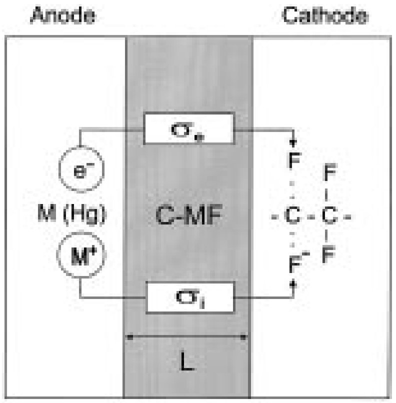


Figure 1. Scheme of the processes occurring at the interface between liquid alkali metal amalgam, M(Hg), and solid poly(tetrafluoroethylene).

Both statements i and ii are elucidated by a model shown in Figure 1. The reaction is initiated by a fast chemical reduction, which produces the first monolayers of C−MF.[55] The product exhibits both electronic[54,56,57] and ionic (M^+)[53] conductivities; i.e., a short-circuited galvanic cell is formed:

$$M(Hg)|C{-}MF|PTFE$$

(The C−MF layer acts simultaneously as a solid electrolyte, electron conductor, and electrode). During the self-discharge, the PTFE carbonization takes place at the carbon (C−MF) cathode, which is continuously renewed in situ as the C−MF layer grows. The cathodic process consists of the splitting of C−F bonds, while the formed F^- anions subsequently recombine with M^+ cations that also passed through the C−MF layer. Assuming for simplicity the cell reaction[58]

$$(-CF_2-) + 2M(Hg)_x \rightarrow (-C-) + 2MF + 2xHg \quad (2)$$

the thermodynamic cell voltage, ΔE equals

$$\Delta E = \frac{\Delta G_{PTFE} - 2\Delta G_{MF} + 2F(E_a - E_0) + 2RT \ln c}{2F} \quad (3)$$

(ΔG denotes Gibbs free energies of formation, F Faraday constant, E_0 standard redox potential of alkali metal (M/M^+), E_a standard redox potential of the amalgam ($M(Hg)/M^+$), and c amalgam concentration). Equation 3 translates (for ΔE in volts and M = Li) into

$$\Delta E = 3.251 + (RT/F) \ln c \quad (4)$$

The current (I) flowing through the cell in Figure 1 can be expressed according to Faraday's law:

$$I = 2SL_0\rho F/tM \quad (5)$$

where S is the area of the PTFE/amalgam interface, L_0 is the thickness of the carbonized PTFE layer, ρ is the density of PTFE, t is time, M is the molar mass of CF_2 unit, and $a = L/L_0$ (L is the thickness of the formed C−MF layer). The current I also obeys Ohm's law, assuming a series combination of ionic (σ_i) and electronic (σ_e) conductivities of C−MF (Figure 1):

$$I = S\Delta E\sigma_e\sigma_i/L(\sigma_e + \sigma_i) \quad (6)$$

Combining eqs 5 and 6 leads to the kinetic equation

$$L_0 = \sqrt{\frac{\Delta EM\sigma_e\sigma_i t}{2aF\rho(\sigma_e + \sigma_i)}} = kt^{1/2} \quad (7)$$

where k is a rate constant. Equation 7 fits the experimental data well,[51,52] and its comparison with eqs 3 and 4 also explains the low sensitivity of k to the amalgam concentration. (For instance, the rate constant, k for $c = 10^{-6}$ atom % still attains ~91% of the value for $c = 1$ atom %). The ΔE values are not much dependent on the type of alkali metal: the amalgam potentials, E_a equal −2.195, −1.959, and −1.975 V for M = Li, Na, and K, respectively.[59] Hence, the rate constant k is practically controlled by the electrical conductivity of C−MF, in which the ionic conductivity, σ_i plays the dominating role.[53]

A more precise mathematical model, proposed by Micka et al.[60] respects (i) the chemical initialization, producing rapidly a thin layer L_1:

$$L_0 = L_1 + kt^{1/2} \quad (8)$$

and (ii) the electrical conductivity of C−MF is also considered a function of time.[60] However, differences between the two models are beyond the usual errors of kinetic measurements. The depicted model of a spontaneously formed local galvanic cell resembles that of the corrosion of metals. Consequently, the term "electrochemical corrosion of PTFE by alkali metal amalgams" also appears.[49,51,52]

Table 2. Electrochemical Carbonization of Fluoropolymers[a]

precursor	reaction conditions	k^a (nm/s$^{1/2}$)	refs
PTFE	Li amalgam	47.5	51, 52
PTFE	Na amalgam	2.67	51, 52
PTFE	K amalgam	0.1	53
PTFE	Pt cathode/DMF−NEt_4BF_4	120^b	22
PTFE	Pt cathode/DMF−NBu_4BF_4	70^b	22, 24
PTFE	Pt cathode/DMF−$NOct_4BF_4$	30^b	22
PTFE	benzoin dianion in Me_2SO	2^b	64
PCTFE	Li amalgam	124	53
Nafion 117	Li amalgam	15.3	46
PTFE−PPVE	Li amalgam	38.3	53
FEP	Li amalgam	47.0	60
FEP	sodium naphthalenide	$0.4^{b,c}$	65

[a] Values of rate constant, k (eq 7) at room temperature (unless stated otherwise). Me = methyl, Et = ethyl, Bu = *n*-butyl, Oct = *n*-octyl. PTFE−PPVE, poly(tetrafluoroethylene-*co*-perfluoropropyl vinyl ether); FEP, poly(tetrafluoroethylene-*co*-hexafluoropropene). For the other acronyms see Table 1. [b] Values estimated from literature experimental data. [c] At 0 °C.

The depicted scheme is applicable also for the amalgam carbonization of various other fluoropolymers[2,46,53] and low molecular weight perhalogenated hydrocarbons[45,47] (cf. Tables 1 and 2). The kinetic model (eqs 3−7) is valid also for liquid or gaseous precursors. However, these systems are sensitive to accidental cracking of the C−MF layer; the precursor subsequently permeates through cracks, which causes uncontrolled acceleration of the kinetics.[2,45,47] A similar effect has sometimes been observed for reactions of solid fluoropolymers with concentrated amalgams at high temperatures, liquid or gaseous alkali metals, or liquid alloys of Na−K.[2,53] For diluted amalgams and lower temperatures (25−100 °C), the "conductivity control" (eq 7) applies perfectly.[2,61]

2. Electrochemical Carbonization in Liquid Electrolyte Solutions. Electrocarbonization may also be realized by "classical" electrochemistry, where the charge-transfer reaction occurs at an interface of metal electrode and liquid electrolyte solution. Figure 2 displays schematically the reductive carbonization of PTFE at a metal cathode.[62] The reduction proceeds at a three-phase interface: PTFE/electronic conductor/ionic conductor.[63] Electrons from the cathode propagate through the growing C−MF phase, while we can distinguish two interfaces: (i) *Outer interface* is in contact with liquid electrolyte solution; the carbonized area propagates rapidly along this interface, since the ion transport in liquid phase is fast. The rate-limiting process is the interfacial charge-transfer reaction.[22,26] (ii) *Inner interface* is equivalent to the interface in the PTFE/amalgam reaction (Figure 1). The kinetics is controlled by the ionic conductivity, σ_i (eq 7); i.e., the measured rate constants, k, are expected to be similar for a given

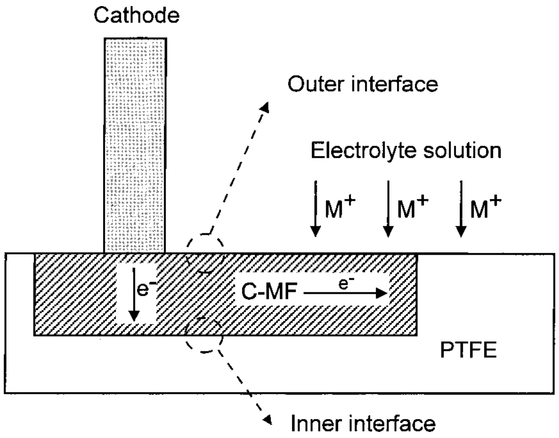


Figure 2. Scheme of the processes occurring at the contact of metal cathode with PTFE in a liquid electrolyte solution.

electrolyte cation, M^+ (cf. Table 2). If the electrolyte solution permeates accidental cracks in C−MF, the model (eq 7) is perturbed and k values increase casually (cf. section I.B.1).

The similarity between the PTFE/amalgam reaction and classical electrochemical reduction of PTFE at metal cathodes was first addressed by Barker et al.[24] On the other hand, any "chemical" defluorination of PTFE must, in principle, proceed electrochemically as well (Figure 1 and eqs 2−7) provided the C−MF is not permeable to the reactants. McCarthy et al. have discussed this mechanism for the reaction of PTFE with benzoin dianion[64] and poly(tetrafluoroethylene-*co*-hexafluoropropene) (FEP) with sodium naphthalenide.[65] Their experimental $L-t$ plots are similar to the corresponding plots for "PTFE/metal−cathode"[22,24] and "PTFE/amalgam",[51,52] which permits the rate constants k to be estimated. Table 2 surveys the rate constants k for some fluoropolymers at room temperature.[22,24,46,51−53,60,64,65] Other relevant values can be found in refs 47, 53, 60, and 66.

Generally, the electrochemical route of carbonization requires the existence of a compact and electrically conducting (both for electrons and ions) interfacial layer of the product, which separates both reactants from a direct ("chemical") contact. This situation occurs almost ideally at the interface of fluoropolymers with diluted alkali metal amalgams.[2] If the interfacial layer is mechanically damaged and the pores are transparent for the reactants, both electrochemical and chemical carbonization is at play.

C. Oxidative Carbonization

There are only a few examples of oxidative carbonization processes; they are mostly connected to the early works on surface-enhanced Raman spectroscopy (SERS). Carbon deposit is formed by photoassisted electrolysis of benzene,[67] pyridine,[14,68−71] 2,2′-bipyridine,[72] 1,10-phenanthroline,[14,68,73] EDTA,[74] 1,2-diaminobenzene, and some other aromatic and aliphatic amines[14,75] at the Ag electrode (for reviews see refs 13, 76, and 77). A possible mechanism starts from anodic oxidation of Ag^0 to Ag^I and subsequent formation of a photosensitive complex with the mentioned molecules and electrolyte anions.[13] Carbon may also be photodeposited at silver surface without any electrochemical promotion; these reactions are sometimes termed "surface-enhanced photochemistry".[78]

On the other hand, the photoassisted route need not be a dominating carbonization process at the electrochemical interface: 1,10-phenanthroline carbonizes at a silver electrode in aqueous chloride medium either photoelectrochemically or (to a larger extent) by a dark charge transfer.[79] Different activated complexes were supposed for photo (9a) and dark (9b) reactions:

$$((\mathrm{Ag^I phen})^+,\mathrm{Cl}^-)_{\mathrm{ads}} \xrightarrow{\text{slow, } h\nu} \mathrm{Ag}^0 + \mathrm{Cl}^- + \mathbf{C} \quad (9a)$$

$$(\mathrm{Ag^0Clphen})_{\mathrm{ads}} \rightarrow \mathrm{AgCl} + \mathrm{phen}^{\bullet -} \rightarrow \mathbf{C} \quad (9b)$$

Dark anodic oxidative carbonization of 1,2-diaminobenzene and some other amines also occurs at the Ag electrode.[14] It was even speculated that the carbon overlayer at silver is the actually SERS-active surface[13,14,67−73,75−77,80,81] promoting adsorption[67,73,80,81] or intercalation[13,72] of the studied molecules. Although the nature of surface enhancement is apparently much more complex, the formation of carbon at certain conditions is well documented (cf. also section II). However, its importance to SERS or photochemistry has never been accepted broadly.

Anodic carbonization of acetylene was reported by Shirakawa et al.[12] The reaction occurs on a Pt anode at 1.5 V vs SCE in the presence of CuCl and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine. It was suggested that the anodic oxidation of acetylene leads to polycondenzation, yielding an sp-bonded polymeric carbon chain ("carbyne"; cf. section VI.B):

$$n\mathrm{H{-}C{\equiv}C{-}H} \xrightarrow{-2(\mathrm{e}^- + \mathrm{H}^+)} (\mathrm{-C{\equiv}C-})_n \quad (10)$$

Although the black carbonaceous product of reaction 10 shows a weak IR band supporting this interpretation ($\upsilon_{\mathrm{C\equiv C}}$ at 2116 cm^{-1}), any deeper characterization of the prepared material is still missing. Analogous catalytic polycondenzation of acetylene or butadiyne[82] (called the Hay, Glaser, or Elington reaction)[11,83] also occurs by the action of oxygen,[11,83,84] iodine,[85] and some other mild oxidants,[86−88] but the products are poorly defined. Chemical and electrochemical polycondenzation of acetylene toward a linear carbon chain (eq 10) was reviewed by Kijima.[11]

II. Electrochemical Carbonization of Carbon Oxides and Carbonates

The formation of elemental carbon by electrochemical reduction of CO_2 and carbonates was first reported in 1964 by Janz and Conte[15] and Delimarskiy et al.[16] Elemental carbon was deposited at −0.47 to −1.17 V vs Ag/Ag^+ on a metal cathode (Pt, Au, Ag, Ni, and Au−Pd alloy) from an eutectic mixture of fused alkali metal carbonates at 600−700 °C purged with CO_2.[15] Carbon was probably formed indirectly (EC mechanism) by a reaction of the electrochemically generated alkali metal, M (reaction 11), with CO_2 (reaction 12) or CO_3^{2-} (reactions 13 and 14):

$$M^+ + e^- \rightarrow M \quad (11)$$

$$4M + 3CO_2 \rightarrow 2M_2CO_3 + \mathbf{C} \quad (12)$$

$$4M + M_2CO_3 \rightarrow 3M_2O + \mathbf{C} \quad (13)$$

$$2M + 2M_2CO_3 \rightarrow 3M_2O + (3/2)O_2 + \mathbf{C} \quad (14)$$

Carbon deposition (reactions 12−14) does not proceed at stainless steel,[89] where passivation takes place. However, at gold or platinum electrodes, electrochemical carbon is formed under almost 100% faradaic efficiency.[16]

The reduction of CO_2 or formate to carbon occurs also at a silver electrode in aqueous electrolyte solution at room temperature.[70,75,80,81] Carbon deposit is formed at −0.2 V vs SCE, and it may further be converted at −1.2 V vs SCE to hydrocarbons by the Fischer−Tropsch reaction:[80,81]

$$CO_2 \rightarrow \mathbf{C} \rightarrow CH_x \quad (15)$$

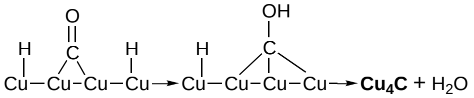
Carbon monoxide is converted to elemental carbon by catalytic disproportionation:

$$2CO \rightarrow CO_2 + \mathbf{C} \quad (16)$$

It yields interesting carbon nanoclusters[90] or nanotubes.[91] Reaction 16 reportedly occurs also in meteorites, being a source of interstellar triply bonded carbon molecules and solids ("carbyne"; cf. section VI.B).[92] Carbon suboxide (C_3O_2) has been reduced to carbon in two steps by bis(bromomagnesium)-acetylide and $SnCl_2$.[93] No systematic attention has been paid to electrochemical carbonization of lower carbon oxides.

Carbonization of CO_2 has been studied in connection with electrochemical CO_2 fixation.[94] The production of hydrocarbons (potential fuels) from CO_2 dissolved in aqueous electrolyte solution depends on the electrocatalytic properties of the electrode material. For instance, Cu, Ag, Sn, and Ti preferentially produce CH_4, CO, HCOOH, and H_2, respectively.[95] Copper was found to be one of the most effective electrode materials for hydrocarbon production, but the evolution of CH_4 and C_2H_4 slows down as soon as the Cu surface is covered by electrochemical carbon.[17−19,95−99] This carbon was assigned as "atomic",[98] "elemental",[17] or "graphitic",[18,95−97] but any in-depth characterization is missing. A pure carbon surface shows very low activity toward the CO_2/CH_x conversion, the main product being hydrogen (at lower pressure of CO_2 and higher current densities) or CO and formic acid (at higher CO_2 pressure and smaller current densities).[100]

Two different mechanisms of copper electrode poisoning by electrochemical carbon have been suggested. According to Cook et al.,[17] a surface carbon layer is formed from chemisorbed carbon monoxide and hydrogen as follows:



(17)

Cu_4C represents surface carbon, which is detectable, e.g., by Auger[17,18] and photoelectron[18] spectroscopy. Contrary to eq 17, Bard et al.[18] have found that chemisorbed CO presents only a minor contribution to the overall rate of poisoning; it is converted to chemisorbed formaldehyde (Cu−HCO), which is then smoothly reduced to hydrocarbons via a surface carbene:

$$CO_2 \rightarrow CO \rightarrow [Cu]\text{−}HCO \rightarrow [Cu]\text{=}CH_2 \rightarrow CH_4 + C_2H_4 \quad (18)$$

(The formation of CH_4 dominates at lower temperatures, whereas the formation of C_2H_4 dominates at higher temperatures). The major route of Cu electrode poisoning by carbon is schematically

$$CO_2 \rightarrow HCOOH \rightarrow \mathbf{C} \quad (19)$$

Formic acid or formate are generated by the addition of $H^\bullet$ or H^- to CO_2. Electrolysis of possible intermediates (CO, HCOOH, HCHO, CH_3OH) at the Cu cathode supports this mechanism; formate rapidly produces carbon, which covers the Cu surface.[18] The electrodeposition of carbon at Cu can be avoided, if the electrode is subjected to anodic pulses superimposed on a cathodic bias (−1.6 to −2.6 V vs Ag/Ag^+, pulses −0.125 V).[19,95] The observed blocking of HCOOH formation supports the mechanism (eqs 18 and 19) as well.

A silver electrode is not poisoned by electrochemical carbon. On the contrary, the CO_2/CH_4 conversion at the Ag cathode is promoted by the intermediate formation of elemental carbon. Silver catalyzes the Fischer−Tropsch reaction; i.e., methane is produced from adsorbed hydrogen and electrochemical carbon (cf. eq 15).[95] This route of CO_2 fixation occurs at potentials below −0.4 V vs Ag/AgCl. At less negative potentials, electrochemical carbon is converted to CO and formate:

$$C + HCO_3^- \rightarrow CO + HCOO^- \quad (20)$$

III. Electrochemical Carbonization of Halogenated Hydrocarbons

A. Reductive Splitting of the Carbon−Halogen Bond

Reductive splitting of the carbon−halogen (C−X) bond at a metal (usually mercury) cathode is a versatile reaction in organic electrochemistry.[48,101,102] The electrochemical carbon−halogen bond fission[48,101−103] is initiated by an electron transfer from the cathode to the halide molecule under formation of an intermediate molecular anion at the electrode, which decomposes slowly under extraction of a halide anion X^- (eq 21). This reaction is rate determining. The $R^\bullet$ formed then triggers fast subsequent radical reactions (e.g., protonization (22a), dimerization (23), coupling, nucleophilic attack, etc.). A second possibility is a two-electron reduction toward a carbanion R^-, which reacts further, for example, with protons (22b).

$$\mathrm{R{-}X} + e^- \rightarrow [\mathrm{R}^{\delta+}\cdots\mathrm{X}^{\delta-}]^- \rightarrow \mathrm{R}^\bullet + \mathrm{X}^- \tag{21}$$

$$\mathrm{R}^\bullet \xrightarrow{\mathrm{H^+(solvent)}} \mathrm{R{-}H}^+ \tag{22a}$$

$$\mathrm{R}^\bullet \xrightarrow{e^-} \mathrm{R}^- \xrightarrow{\mathrm{H^+(solvent)}} \mathrm{R{-}H} \tag{22b}$$

$$2\mathrm{R}^\bullet \rightarrow \mathrm{R{-}R} \tag{23}$$

The actual mechanism is precursor dependent, but the first case (one-electron process) prevails. For instance, perfluoroalkyl iodides yield exclusively the corresponding perfluoroalkyl radicals; only CF_3Br gives a mixture of radical and carbanion $CF_3^\bullet/CF_3^-$.[104] Electrolytic reduction of monohalides RX (R = alkyl) in protic solvents leads to the corresponding hydrocarbons RH (eqs 22a and 22b) and, to a lower extent, also to a dimeric product, RR (eq 23). Even a very weak acid can serve as a source of protons, e.g., dimethylformamide or acetonitrile, which are thus converted to $CON(CH_3)_2^-$ or CH_2CN^-.[105,106] Since the rate-determining reaction (21) does not involve protons, the kinetics of C−X bond splitting is usually pH-independent in protic solvents. An exception is the C−F bond, where protons form a hydrogen bond-activated complex (cf. eq 21):

$$[\mathrm{R}^{\delta+}\cdots\mathrm{F}^{\delta-}\cdots\mathrm{H}^+]$$

This assists the electrode in the polarization of the C−F bond.[107] Reducibility of the C−F bond depends also considerably on the nature of the fluorocarbon molecule.[108,109] Richmond et al.[110] have reviewed the activation and splitting of C−F bonds by metal complexes. Protonization of the intermediate radicals/anions (eqs 22a,b) apparently blocks the electrochemical carbonization, since hydrocarbons are no more reducible to elemental carbon.[111] Therefore, electrochemical carbon is formed from carbon halides only in perfectly aprotic media, e.g., in cells with solid electrolytes.

B. Low Molecular Weight Carbon Halides

1. Carbon Tetrahalides. Reductive carbonization of CCl_4, CBr_4, and CI_4 with mercury at high temperature was first reported by Tammann in 1921;[112] he did even speculate about the formation of a new carbon allotrope, other than cubic diamond or graphite. Analogously, Holcombe et al.[113,114] have claimed a synthesis of lonsdaleite (hexagonal diamond) and other unusual carbon allotropes ("carbon VI", "chaoite", and "carbyne") via the reduction of carbon tetrafluoride with Si, SiC,[115] and CH_3SiCl_3 at high temperatures. A quantitative low-temperature carbonization of CCl_4 by sodium amalgam was first reported by Fetkenheuer in 1923.[118] On the other hand, CF_4 (also C_2F_6) does not react markedly with alkali metal amalgams at 25−150 °C.[45] This contrasts with the behavior of higher perfluoro-*n*-alkanes (section III.B.4).[45]

Burdeniuc and Crabtree[119] have reported an interesting quantitative (95−100%) carbonization of CCl_4, $CFCl_3$, and CF_2Cl_2 by the action of solid sodium oxalate at 270−290 °C:

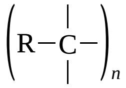
$$\mathrm{CF}_x\mathrm{Cl}_{4-x}(\mathrm{g}) + 2\mathrm{Na_2C_2O_4}(\mathrm{s}) \rightarrow x\mathrm{NaF}(\mathrm{s}) + (4-x)\mathrm{NaCl} + \mathrm{C}(\mathrm{s}) + 4\mathrm{CO_2}(\mathrm{g}) \tag{24}$$

Reaction 24 is applicable also to other saturated perhalocarbons; i.e., it permits a liquidation of these environmentally hazardous molecules. Elemental carbon was isolated in stoichiometric amounts,[119] but its in-depth characterization is missing.

Mechanistic details about the reduction of carbon tetrahalides by oxalate (Hg, amalgams) are unknown, but the reaction may well be electrochemical in nature (section I.B). A "classical" electroreduction of carbon tetrahalides, e.g., on a mercury cathode in dimethylacetamide or acetonitrile, yields usually dihalocarbene, $:CX_2$, and, subsequently, dihalocarbene dianion, $:CX_2^{2-}$ which can be trapped, e.g., by a reaction with olefins; otherwise it is protonated to CH_2X_2.[105] Analogously, photoreduction of CCl_4 on illuminated TiO_2 yields carbene, $:CCl_2$, and $^\bullet CCl_3$ radical, which may be further hydrolyzed to CO, CO_2, and HCl.[120]

Sailor et al.[42] have reported reduction of CCl_4 to "carbonaceous fibers" at Ni, Cu, Ag, Pt, and Fe cathodes in acetonitrile or dichloromethane solutions of NBu_4BF_4 (Bu = *n*-butyl) or bis(triphenylphosphoranylidene)ammonium chloride. The product was not pure elemental carbon; it contained residual chlorine and encapsulated solvent molecules. The most interesting feature was the fibrous morphology of the product. The fibers were ∼5 μm in diameter, and they showed pronounced striations parallel to the long axes. Raman spectra indicate a structure of disordered, sp^2-bonded carbon material similar to that of glass-like carbon.[121]

Substituted carbon tetrachlorides, $RCCl_3$ (R = H, methyl, phenyl), are reducible by Na/K alloy[122,123] or $M(biphenyl)_2$ (M = Ca, Ba, Sr)[124] only to RC, since the C−H and C−C bonds are inert against reductive splitting. The product, called poly(alkylcarbyne), represents an interesting three-dimensional sp^3 carbon network:[122,123,125,126]



$$\left(\mathrm{R}{-}\overset{|}{\underset{|}{\mathrm{C}}}{-}\right)_n$$

Pyrolysis of $(RC)_n$ yields predominantly sp^3 (diamond-like) carbons.[122,123]

2. Hexachlorobuta-1,3-diene. Nishihara et al.[38−41,127,128] reduced hexachlorobuta-1,3-diene at a carbon electrode in NBu_4BF_4/CH_3CN. The product was electroactive carbon (graphite) film, and it was reversibly dopable under insertion of both cations and anions. The electrochemical doping/undoping was evidenced by a continuous growth of a reversible redox wave during the film formation (Figure 3a). This wave was centered at −0.4 V vs Ag/Ag^+, and it persisted at potential sweeps more positive than the carbonization potential (−1.8 V vs Ag/Ag^+; Figure 3b). However, the carbonization was not complete as the produced graphite contained some residual chlorine.[39] Shirakawa et al.[11,36,37] have studied the same reaction in NBu_4ClO_4/dimethylformamide. In contrast to the earlier work,[39] they have found that the produced carbon is not solely graphite, but it also contained considerable amount of triply bonded (carbyne-like)

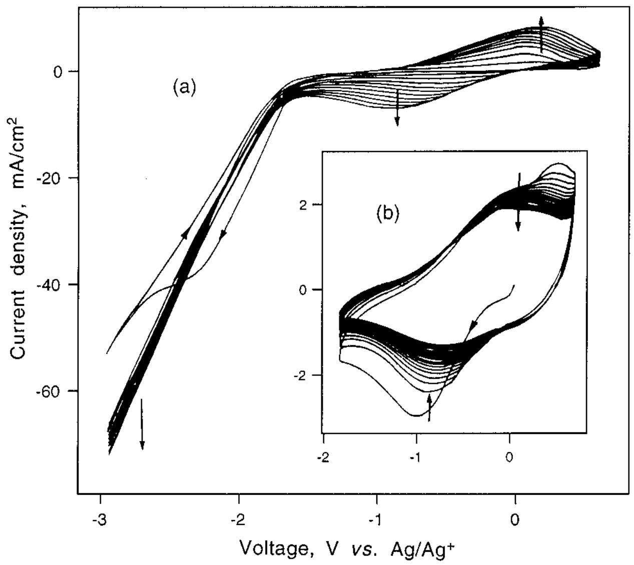
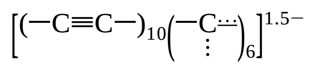


Figure 3. Cyclic voltammetry of 0.16 mol/L hexachlorobuta-1,3-diene on glass-like carbon electrode in 0.1 mol/L NBu_4BF_4 + acetonitrile at a scan rate of 150 mV/s (a). Inset (b) shows cyclic voltammogram of the carbonaceous film grown in (a) after the vertex potentials were switched to values more positive than the potential of carbonization. Arrows (↑↓) indicate the directions of increase or decrease in current values by successive potential scans. Adapted with permission from ref 39. Copyright The Royal Society of Chemistry.

carbon. On the basis of the results of chemical analysis, IR, Raman, ^{13}C NMR, and EPR, the product was formulated as n-doped all-carbon polymer, containing acetylenic sp carbons and cumulenic sp and aromatic sp^2 links:



$$\left[(-C{\equiv}C-)_{10}\left(-\overset{}{\underset{\vdots}{C}}\cdots\right)_{6}\right]^{1.5-}$$

3. Diiodoacetylene. Shirakawa et al.[11,34,35] reduced diiodoacetylene to carbon at a platinum electrode at −0.2 V vs SCE in dimethylformamide containing Bu_4NClO_4, Bu_4NI, Me_4NClO_4 (Me = methyl), $NaClO_4$, and NaCl. The reaction is catalyzed by $NiCl_2$[1,3-bis(diphenylphosphino)propane] and NiI_2-[1,2-bis(diphenylphosphino)ethane].[129] It was suggested that this reaction may lead to a sp-bonded carbon allotrope ("carbyne"):

$$n\mathrm{I{-}C{\equiv}C{-}I} \xrightarrow[-\,\mathrm{I}^-]{e^-,\ \text{Ni cat.}} (-\mathrm{C{\equiv}C}-)_n \qquad (25)$$

However, the product also contained H, N, I, and Ni,[34] and the X-ray diffraction showed only the usual pattern of sp^2 carbon (graphite-like).[34,35]

4. Perfluorinated Hydrocarbons. Electrochemical reductive carbonization of perfluorinated coronene ($C_{24}F_{36}$),[130] perfluoroanthracene ($C_{14}F_{24}$), perfluorodecacylene ($C_{36}F_{54}$), perfluorophthalocyanine ($C_{32}F_{56}N_8$), and perfluoroparacyanogene ($CFN_{2.2}$) in $LiClO_4$ + propylene carbonate was reported, but in-depth characterization of the products is missing.[131] Analogously, the reduction of perfluorodecalin ($C_{10}F_{18}$),[132] perfluoro-*n*-alkanes, C_xF_{2x+2} ($x = 6, 8$),[133,134] and perfluoro-2,4-dimethyl-3-ethylpentane (C_9F_{20})[133,134] in acetonitrile, dimethylformamide, or dichloromethane media does not lead to defined products: they were identified as partially defluorinated, unsaturated polymers, also containing C−H and C=O bonds.[133]

Quantitative defluorination of perfluorinated hydrocarbons and similar compounds occurs by the action of alkali metals[135] or sodium biphenyl;[136] these reactions do not lead to simple products, either, but the process has found application for mineralization of organic fluorides in analytical chemistry.[135,136] A complete defluorination of perfluorodecalin by arylthiolates proceeds under controlled conditions to octakis(arylthionaphthalene).[137]

Defined carbonization by defluorination of perfluorobenzene and perfluoro-*n*-alkanes C_xF_{2x+2} ($x = 6, 9, 20, 24$) can be achieved by alkali metal (Li, Na, K) amalgams.[45,47] The amalgam carbonization is conditioned by a perfect electrical contact between the product (C−MF, growing on top of the M(Hg) surface) and the precursor (fluorocarbon). This is obtained, for example, by continued apposition of the precursor from liquid or gaseous phases or by the polymeric nature of the precursor (section III.C−F).[45]

Fluorinated fullerenes $C_{60}F_x$ and $C_{70}F_y$ ($x \approx 45$, $y \approx 54$) are electrochemically reducible at more positive potentials (by 1.3−1.6 V) than the parent fullerenes.[138] The cleavage of the C−F bond occurs after a reversible three-electron reduction of $C_{70}F_{54}$ (EEEC mechanism).[138]

5. Halogenated Adamantane. Kasatochkin et al.[139] have reported preparation of a white carbon material (~99% C) by dehydrohalogenation of 1,3,5,7-tetrabromoadamantane by sodium suspended in xylene (Wurtz reaction) and have declared the product as "dehydropolycondenzed adamantane". However, trials to reproduce this work failed: the reaction led to a network of broken C_{10} units and short hydrocarbon chains, which reverts to graphite upon heat treatment.[140]

C. Polycarbon Fluoride (Fluorographite)

Electroreduction of polycarbon fluorides (fluorographites) $(CF_x)_n$ ($x \leq 1$)[141,142] has been studied extensively since 1968[143] in connection with primary lithium batteries.[43] Consequently, the experiments have usually been carried out in a cell with lithium anode, composite cathode (a mixture of $(CF_x)_n$ with a conductive binder), and a liquid or solid[144] Li^+ electrolyte.

The reduction of $(CF_x)_n$ is not a simple defluorination to LiF and elemental carbon. The $(CF_x)_n$/Li cells show an open circuit voltage of about 3.2−3.5 V, which is substantially lower than the thermodynamic value (4.57 V). The discrepancy was discussed[131,145] in terms of a mixed potential with participating redox reactions of the solvent. A nonstoichiometric ternary intercalation compound (with co-inserted solvent molecule, S)[146,147] is formed as a primary product:[148]

$$(CF_x)_n + nx\mathrm{Li} + ny\mathrm{S} \rightarrow (\mathrm{CLi}^+_x\mathrm{F}^-_x\mathrm{S}_y)_n \qquad (26a)$$

It further decomposes to elemental carbon (graphite):

$$(\mathrm{CLi}^+_x\mathrm{F}^-_x\mathrm{S}_y)_n \rightarrow xn\mathrm{LiF} + yn\mathrm{S} + \mathbf{C}_{\boldsymbol{n}} \qquad (26b)$$

Therefore, the overpotential of $(CF_x)_n$ reduction is not caused by activation polarization of the cathode but by a slow Li^+ transport in the ternary intercalate formed. The poly(dicarbon monofluoride), $(C_2F)_n$, shows a lower cathode overpotential (faster Li^+ transport) due to a more disordered crystal structure of the precursor.[149] If Li^+ is replaced by NBu_4^+, the cation transport slows down and the reduction is more difficult.[150] The electrochemical carbon (graphite) from the $(CF_x)_n$ defluorination does not attract much attention; i.e., a deeper review is beyond the scope of this article.

D. Poly(tetrafluoroethylene)

PTFE and other perfluorinated polymers are known for their extraordinary chemical and thermal stability. Pyrolysis does not yield any carbon but low molecular weight fragments with a dominating proportion of the monomer.[151] Pyrolytic polymeric carbon can only be prepared from partially halogenated polymers such as poly(vinylidene fluoride) (PVDF).[152] Analogously, PVDF gives higher yields of carbonaceous products upon ion bombardment;[153,154] laser ablation of poly(tetrafluoroethylene-*co*-ethylene) produces considerable amounts of ionized fullerene C_{60}^+.[155]

Nevertheless, PTFE is thermodynamically very unstable against reductive defluorination. A hypothetical reaction:[156−159]

$$(-CF_2-) + H_2 \rightarrow (-C-) + 2HF \qquad (27)$$

corresponds to $\Delta G_0 = -193.18$ kJ/mol, which translates into the standard redox potential:

$$E_0 = -\Delta G_0/2F = 1.00\ \mathrm{V} \qquad (28)$$

Therefore, the apparent chemical stability of PTFE is only a kinetic one, and PTFE should be carbonizable even with very mild reductants. All these reactions can, at least theoretically, be regarded as electrochemical processes (cf. section I.B).

Formation of metallic fluorides was reported during the contact of PTFE (and/or some other perfluorinated polymers) with metals: Ni,[160] Al,[161−164] Cr,[161−163] Cu,[161,162] Cd,[162] Pb,[163] In,[165] Ti,[161,162] Zn,[163] Sn,[165] Na,[166,167] and stainless steel[160] (for a review of fluoropolymer metallization, see ref 168). The contact is usually made by vacuum deposition of a thin metal layer at PTFE. The defluorination is not complete even with the sodium vapor.[166,167] This reaction yields crystalline NaF and a complicated unsaturated and cross-linked polymer, whose composition also depends on the reaction time.[166,167] Only a prolonged exposure of PTFE to alkali metals or their alloys[45,53,169] seems to lead to pure carbon. The mechanistic details are unknown; presumably both electrochemical and chemical pathways are to be considered.[45,53,166]

Most of the carbonization studies were carried out with as-received commercial PTFE samples (duPont's Teflon). Mechanically oriented foils[26,45] and highly oriented films prepared by friction deposition[170] were also tested.[171] The latter seem to be particularly interesting precursors of electrochemical carbon, as they show a perfect orientation of individual PTFE macromolecules.[172−176] Whether or not this orientation is preserved in the followup electrochemical carbons is, however, not yet confirmed.[167,171] Some orientation was apparent on electrochemical carbon from oriented foils.[26,45]

1. Reaction of PTFE with Alkali Metal Amalgams. Complications due to incomplete defluorination[166,167] can be avoided if pure alkali metals are replaced by dilute liquid alkali metal amalgams.[49−53] (For a survey of electrochemical properties of alkali metal amalgams, see ref 59). Basic features of the PTFE/M(Hg) reaction have already been discussed in section I.B. Compared to alternative electrochemical carbonizations, there are three main advantages of the amalgam carbonization: (i) The defluorination is quantitative, independently of the reaction temperature (down to sub-room temperatures),[53] amalgam concentration, and reaction time (L_0 values).[52,53] (ii) Any common impurities (e.g., H and O from solvents and air) are safely excluded. (iii) The reduction rate is well controlled (eq 7) by only two variables, temperature and the type of alkali metal.[52,53]

2. Reaction of PTFE with Solvated Electrons and Anion Radicals. PTFE reacts with ammonia solutions of alkali metals[177−180] and Mg[181] in which solvated electrons are assumed to exist. The defluorination is usually incomplete; the products also contain C−H bonds since NH_3 acts as a proton donor (cf. eqs 22a and 22b). (It is even questionable whether some products can still be considered as "carbon".[182]) ESCA,[177,179−181] infrared and soft X-ray spectroscopy,[179] and reactions with bromine[177] and other reagents[178] lead to a picture of a disordered unsaturated polymer that reacts with oxygen and moisture to form C=O and COOH groups. The main application consists in the promotion of bondability of PTFE (for reviews, see refs 168 and 183−187).

The reaction of PTFE with Li/NH_3 yields a variety of products depending on the molar ratio of reactants.[182] At $Li/CF_2 \leq 2$, the products were black-gray, brittle and insoluble solids (of composition $C_3H_2F_3$ and $C_{72}H_{113}F_{20}$). At $Li/CF_2 = 4$, the product was identified as a high-density and high molecular weight polyethylene:[182]

$$(-CF_2-) + 4Li + 2NH_3 \rightarrow (-CH_2-) + 2LiF + 2LiNH_2 \qquad (29)$$

The solution of Mg in NH_3 is a milder defluorinating agent for PTFE than the solutions of alkali metals in NH_3.[181] (The reactant was prepared electrochemically by dissolution of a Mg anode in the solution of NH_4BF_4, as Mg is normally insoluble in NH_3.) Thicknesses of the magnesium-modified layer are only between 15 nm and 1 μm; i.e., the polymer becomes hydrophilic without noticeable color change.[181]

The reaction of sodium naphthalenide ($NaC_{10}H_8$, also called "sodium naphthalide", "sodium naphthalene", or "sodium dihydronaphthylide" (IUPAC term))[188] with perhalogenated polymers is again mainly applied for the adhesion enhancement of fluoroplastics.[183,187,189−195] Industrial naphthalenide preparations (from W. L. Gore Associates, Inc., or Matheson Gas Products) are called Tetra-Etch; other commercial names are Fluor-Pick ST 18, Fluorotech, Bondaid, Fluorobond, Chemgrip, etc.[196] Fundamental patents, safeguarding surface treatment of fluoroplastics by solutions of alkali metals, were granted to Du Pont and Minnesota Mining & Mfg. Co. in 1957−8.[193,197,198]

The kinetics of the R−X (R = alkyl) bond splitting by naphthalenide was studied in detail.[188,199] The reactant is usually prepared from sodium metal and naphthalene in tetrahydrofuran, but it can be also generated electrochemically in a solution of naphthalene in dimethylformamide + NBu_4BF_4 or NBu_4ClO_4 at −2.45 to −2.6 V vs SCE.[27,200] This apparently avoids dangerous work with sodium.

Since the reduction of PTFE regenerates the starting naphthalene (30b), the reaction may propagate catalytically in the presence of substoichiometric amounts (5−10%) of naphthalene:

$$C_{10}H_8 + e^- \rightarrow {}^{\bullet}C_{10}H_8^- \qquad (30a)$$

$${}^{\bullet}C_{10}H_8^- + 0.5\,(-CF_2-) \rightarrow 0.5(-C-) + F^- + C_{10}H_8 \qquad (30b)$$

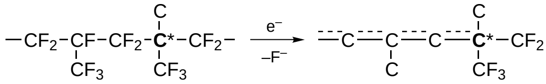
The catalytic cycle is driven (in 30a) either electrochemically[27,200] or through the reaction with excess alkali metal. A similar scheme is applicable to reactions with radical anions (${}^{\bullet}R^-$) derived from pyrene, benzanthracene, phenanthrene, triphenyl, benzpyrene, 9,10-dimethylanthracene, acenaphthalene, fluoranthene, perylene, biphenyl, benzophenone, and triphenylborane.[201,202] The reaction rate increases with decreasing redox potential of the $R/{}^{\bullet}R^-$ couple and also in the sequence K < Na < Li. If the reaction is carried out in a strictly aprotic medium, the carbonaceous product contains only a small amount of heteroatoms.[201,202]

Short-time reaction of PTFE with naphthalenide yields a conducting polymer of the composition $(CF)_n$, which was formulated as a poly(perfluoroacetylene).[203,204] Although the electrical properties of $(CF)_n$ are similar to those of polyacetylene, no other supporting arguments were given. The preferential formation of $(-CF{=}CF-)_n$ links occurs at low temperature (−40 °C).[205] After a longer reaction time, this hypothetical product converts to carbon and NaF.[203,206] Analogously, an almost quantitative defluorination takes place with poly(tetrafluoroethylene-*co*-hexafluoropropene).[65]

The carbonized layer on top of PTFE and other fluoropolymers can be removed by strong oxidants, which yield a carboxylic acid-functionalized fluoropolymer surface.[207] Anchoring of polypyrrole allows preparation of patterned conductive polymer coatings on PTFE.[208] A more sophisticated technique of patterned coating consists in the irradiation of PTFE with X-ray photons (35−1486 eV)[209−218] or electrons (∼0.13−4 keV),[209−211,217−219] which causes a dramatic decrease of the fluoropolymer reactivity toward carbonization with sodium naphthalenide.[220]

Rutherford backscattering spectroscopy indicates that the carbonization rates for virgin and preirradiated PTFE differ by 2 orders of magnitude.[209,215] Selective carbonization of the PTFE surface after patterned irradiation presents a useful photolithographic technique.[214] It can be further upgraded by deposition of Cu onto the carbonized pattern, either by selective chemical vapor deposition[212,218] or electroless deposition.[209,217,221] These studies lead to promising applications in electronics, e.g., for high-frequency (>30 MHz) integrated circuits.[221]

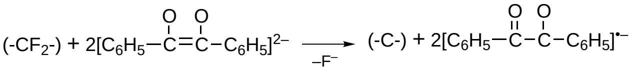
XPS[210] and photostimulated desorption[213,219] evidence that cross-linking and branching of the irradiated PTFE is responsible for its decreased carbonization ability.[222] However, relations between the cross-linking/branching and the carbonization rate of PTFE were not elucidated clearly. One possible interpretation was suggested by Doblhofer et al.,[66] who found similar carbonization blocking in a plasma-polymerized hexafluoropropene. Assuming an electrochemical mechanism (section I.B), the electron propagation along the chain should stop at the cross-linked center (**C***):



$$-CF_2-\underset{CF_3}{CF}-CF_2-\underset{CF_3}{\overset{C}{\mathbf{C}^*}}-CF_2- \xrightarrow[-F^-]{e^-} \overline{\overline{\cdots}}C\overline{\overline{\cdots}}\underset{C}{C}\overline{\overline{\cdots}}C\overline{\overline{\cdots}}\underset{CF_3}{\overset{C}{\mathbf{C}^*}}-CF_2- \qquad (31)$$

because the $C_4\mathbf{C}^*$ units (C−C bonds) are not reductively splitted.[223]

The reduction of PTFE with benzoin dianion was described by Costello and McCarthy:[64,224]



$$(\text{-}CF_2\text{-}) + 2[C_6H_5-\overset{O}{C}{=}\overset{O}{C}-C_6H_5]^{2-} \xrightarrow[-F^-]{} (\text{-}C\text{-}) + 2[C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{O}{C}-C_6H_5]^{\bullet-} \qquad (32)$$

The product was a silver- or gold-colored carbonaceous layer which turned white upon oxidation with air, O_2, or $KClO_3$. It was identified as a cross-linked polymeric carbon containing single, double, and triple bonds, F, H, and small amount of O.[64] This is in contrast to the conclusion of Iqbal et al.[225] that reaction 32 produces only low yields of carbon, the major product being *trans*-polyacetylene, $(CH)_x$. Reaction 32 was applied for selective metalization of PTFE and various other fluoropolymers.[226]

Partial photoinduced defluorination of PTFE[227−230] and other saturated perfluorocarbons[227,231,232] by ammonia,[227,228] hydrazine,[229,230] and other electron donors[231,232] was also reported. Extensive defluorination of PTFE occurs by photoassisted reduction with disodium salt of 3-mercapto-2-butanol and some other thiolates.[233] These reactions may also be applicable for patterned coating and metalizing of PTFE.[228−230,233]

3. Reduction of PTFE in Electrochemical Cells. Direct cathodic reduction of PTFE was first demonstrated by Gabano et al.[20] in a cell with lithium anode, a composite cathode containing PTFE powder + graphite, and a solution of $LiClO_4$ or $LiBF_4$ in tetrahydrofuran, dioxolan, dimethoxyethane, or diethylene glycol. The Li|PTFE cell delivered, at ∼1 V and ∼100 Ω load, almost the theoretical faradaic charge corresponding to complete defluorination of PTFE. Quantitative carbonization of a PTFE/graphite composite also takes place in cells with poly(ethylene oxide)-based solid electrolyte at 1−1.5 V vs M/M^+ (M = Li, Na) and 58−82 °C.[234] These systems were suggested as primary lithium batteries.[20,234] Although PTFE exhibits a very attractive theoretical faradaic capacity (1.07 A·h/g, eq 27), the Li/PTFE

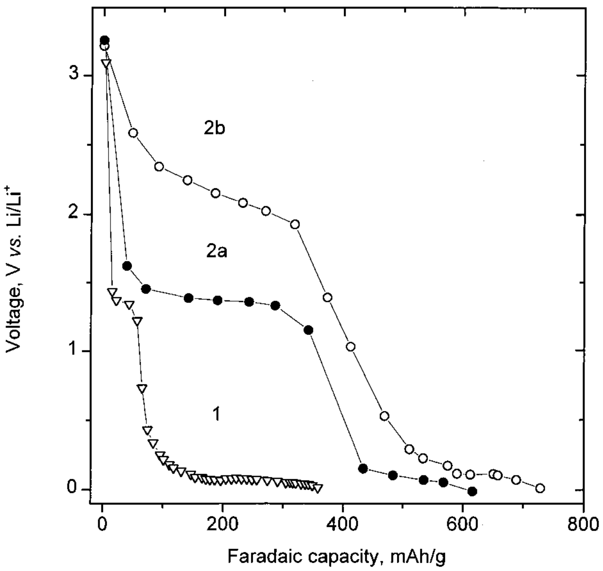


Figure 4. Electrochemical titration curves of PTFE/carbon composites in $LiPF_6$ + ethylene carbonate/diethylene carbonate (50/50 v/v). The composite containing 0.47 wt % PTFE (1) or 32.6 wt % PTFE (2a and b) was galvanostatically prereduced at 0.5 mA/cm^2, while the potentials were recorded after 23 h (1, 2a) or 30 days (2b) of equilibration at open circuit conditions. Reprinted with permission from ref 21 Copyright 1996 Elsevier Science B.V.

cells are inferior because of slow kinetics and lack of rechargeability.

The PTFE/graphite composite is widely used as a negative electrode in modern lithium ion batteries; however, this system is inherently sensitive to capacity loss due to the PTFE electrocarbonization mentioned above. Cheng et al.[21] have demonstrated, in accordance with refs 20 and 234, a complete carbonization of PTFE in $LiPF_6$ + ethylene carbonate/diethylene carbonate (50:50 v/v) solution. Figure 4 displays the electrochemical titration curves of two PTFE/graphite composite electrodes containing 0.47 wt % of PTFE (curve 1) and 32.6 wt % (curves 2a and 2b) of PTFE. The potentials were recorded after galvanostatic reduction to a desired faradaic capacity and subsequent 23 h (curves 1 and 2a) or 30 days (curve 2b; the steady-state values) of equilibration at open-circuit conditions. The difference between curves 2a and 2b (Figure 4) indicates that the carbonization mechanism includes two parallel reactions: besides the direct cathodic carbonization of PTFE at three-phase interfaces (Figure 2), there is a second possible reaction, which is triggered by the intermediate formation of Li/graphite intercalate Li_mC (or even metallic Li), and this subsequently reduces PTFE chemically:

$$Li_mC + x(-CF_2-) \rightarrow Li_{m-2x}C + x(-C-) + 2xLiF \quad (33)$$

The experimental faradaic capacity of PTFE (1.2 mA·h/g, cf. Figure 4) even exceeded the theoretical value (1.07 A·h/g, eq 27) which was attributed to the parasitic breakdown of the electrolyte solution. However, there might be also another interpretation (not mentioned in ref 21): Assuming the natural n-doping of electrochemical carbon (see section IV.A), the theoretical faradaic capacity of PTFE rises to 1.28 A·h/g (for a typical doping level of 0.2), which is close to the experimental value reported.[21]

Reductive carbonization of a pure PTFE film contacting a lead–antimony cathode in a solution of NBu_4BF_4 in dimethylformamide was first reported by Brewis et al.[200] This reaction at platinum or glass-like carbon electrodes[235] was further studied in detail by this[22–26,236] and other groups.[27–30,62,237–239] Coulometric experiments indicate a complete defluorination of PTFE, i.e., a consumption of 2.05–2.45 electrons per $-CF_2-$ group.[22,24,25] (Again, there is a small superstoichiometric electron consumption due to doping; cf. section IV.A.)

The reduction of PTFE starts at ~−1.5 V vs SCE, and the carbonized area propagates in all directions from the contact point (cf. Figure 2).[63] Its shape depends on the preparation history of a PTFE sample: the electrochemical propagation proceeds rapidly along the chains in mechanically oriented PTFE foils (anisotropic carbonization).[22,26] However, the surface propagation stops as soon as the iR drop along the surface compensates the required reduction overpotential.[22] The reaction can then propagate only into the bulk, where the ohmic losses are negligible at common foil thicknesses.[22] This propagation is slow, since the formal diffusion coefficient of NBu_4^+ in $C-NBu_4F$ is only ~10^{-13} cm^2/s.[24] With increasing size of the NR_4^+ cation (R = Et, Bu, Oct), the carbonization rate drops[22] (Table 2). However, the onset potential of PTFE reduction surprisingly shifts to less negative values in the same series.[28,132] The surface and bulk carbonization can be distinguished chronoamperometrically.[22,24]

E. Poly(chlorotrifluoroethylene)

Due to the lability of C–Cl bond, poly(chlorotrifluoroethylene) (PCTFE) shows easier reductive dehalogenation than PTFE and sometimes also different products.[225] For instance, reduction with benzoin dianion yields carbon,[225,226] whereas PTFE gives at the same conditions, reportedly, polyacetylene[225] (cf. section III.D). The reaction with alkyllithium leads primarily to a substitution of Cl, but subsequent loss of fluorine atoms gives a substituted polyacetylene: $(-C(R)=CF-)_n$,[207,240,241] which can be further modified chemically.[242,243]

PCTFE is smoothly carbonized by lithium amalgam (cf. Table 2).[53,244] Direct cathodic reduction of PCTFE in γ-butyrolactone solutions of $LiBF_4$ and/or $NaBF_4$ has been interpreted in terms of a catalytic cycle including electrolyte cations (Li^+, Na^+). Chronopotentiometric measurements show that the cations not only carry the charge down to the virgin PCTFE (cf. Figure 2) but also react reversibly with the intermediates according to the general scheme:[31,32,245]

$$-CX_i- \xrightarrow{e^-} [-CX_i-]^{\bullet-} \xrightarrow{M^+} [-CX_iM-]^{\bullet} \xrightarrow[-MX]{} [-CX_{i-1}-]^{\bullet}\ (0 \le i \le 2) \quad (34)$$

The carbonization rate is higher for amorphous PCTFE than for the crystalline polymer; the charge-transfer coefficient being 0.22 and 0.17, respectively.[246] Irradiation of PCTFE with γ-photons (^{60}Co) impedes the reductive carbonization.[247] Although the original interpretation was different,[247] this resembles the effects of electrons and X-ray photons on PTFE (section III.D).

F. Other Halogenated Polymers

Perhalogenated polymers[248,249] react with alkali metal amalgams analogously to PTFE and PCTFE. Quantitative data exist for poly(tetrafluoroethylene-*co*-hexafluoropropene, FEP),[60,66] Nafion 117 (duPont's trade mark),[46] poly(tetrafluoroethylene-*co*-perfluoropropylvinylether),[53] and liquid perfluoropropenoxide.[53] Also briefly mentioned were Fluoropak 80 (The Fluorocarbon Co., Fullerton, CA), Teflon 6 (duPont), Ribbon Dope-P-412 (Permacel, New Brunswick, NJ),[244] and Nafion 125 and Nafion 901 (duPont).[46] The presence of a limited number of heteroatoms (oxygen in etheric groups, sulfonic groups) decreases the reaction rate, but the C−F bond splitting is still quantitative. Sulfonic groups in Nafions are not reduced; this allows synthesis of sulfonated carbon materials.[46]

On the other hand, partially halogenated polymers such as PVDF, poly(vinyl chloride) (and also polyethylene) do not react with amalgams even at enhanced temperatures (150 °C).[53] This is probably caused by the presence of nonreducible C−H bonds, which block the formation of conjugated carbon−carbon bonds and the growth of a conductive carbon skeleton. (Reductive splitting of C−H bonds to C + H^- occurs only under drastic conditions: polyacetylene is carbonized with potassium at 800 °C and 20−40 kbar.[250]) PVDF is also completely inert against direct electrolysis at a carbon cathode.[33,239] Copolymers of tetrafluoroethylene and vinyl fluoride show behavior intermediate between that of PTFE and PVDF.[239]

Poly(vinyl halides) are, however, chemically dehydrohalogenated in alkaline media:[251−255]

$$-\mathrm{CH_2}{-}\mathrm{CX_2}- \xrightarrow{-\mathrm{HX}} -\mathrm{CH{=}CX}- \xrightarrow{-\mathrm{HX}} -\mathrm{C_2}- \tag{35}$$

An analogous reaction proceeds with a copolymer of vinylidene fluoride and tetrafluoroethylene[256] and poly(trichlorobutadienes).[257] The carbonization (35) accelerates in the presence of phase-transfer catalysts (quaternary ammonium or phosphonium halides),[207,255,256,258] but it can be also driven electrochemically. Shirakawa et al.[33] found that reductive carbonization of PVDF dissolved in dimethylformamide + NBu_4ClO_4 takes place at a Pt cathode, provided *tert*-butyl alcohol (BuOH) is added to the electrolyte solution. The catalytic cycle is schematically depicted as follows:

$$\mathrm{BuOH} \xrightarrow{\mathrm{e^-\ (Pt\ cathode)}} \mathrm{BuO^-} \tag{36a}$$

$$-\mathrm{CH_2}{-}\mathrm{CX_2}- \xrightarrow[-(\mathrm{X^-} + \mathrm{BuOH})]{\mathrm{BuO^-}} -\mathrm{CH{=}CX}- \xrightarrow[-(\mathrm{X^-} + \mathrm{BuOH})]{\mathrm{BuO^-}} -\mathrm{C_2}- \tag{36b}$$

The product also contains (besides some residual F and H) inserted NBu_4^+; i.e., it is naturally n-doped by electrochemical overreduction (cf. section IV.A). The chemical dehydrohalogenation of poly(vinylidene halides) (eq 35) does not lead to n-doping.

Even in the absence of BuOH, reactive nucleophiles like $[(CH_3)_2NCHO]^-$ or $(CH_3)_2N^-$ can also be generated by pre-electrolysis of pure electrolyte solutions.[239] These nucleophiles react with PVDF to eventually give carbon (eq 36b). Under the same conditions, PTFE shows no reactivity[239] and poly(vinyl chloride) is dehydrohalogenated only to $(-CH{=}CH-)_n$.[259−262] Carbon is formed by dehydrochlorination of chlorinated polyacetylene[263] and chlorinated poly(vinyl chloride)[264−266] (both formulated as $(CHCl)_n$).

Apparently, reductive carbonization at metal cathodes proceeds either directly or indirectly (EC mechanism). Perhalogenated polymers show both direct reduction[20,22−26,29,234,237−239,267] and indirect reduction,[27,200] but partly halogenated polymers are electroreduced only indirectly via suitable mediators.[11,33,239]

IV. Chemical Properties of Electrochemical Carbon

A. Doping by Reduction

Reductive carbonization of perhalogenated hydrocarbons (eq 37) is generally accompanied by a small superstoichiometric consumption of electrons (eq 38), which is considered as n-doping of electrochemical carbon:[268]

$$\mathrm{CX}_i + i\mathrm{e}^- \rightarrow \mathrm{C} + i\mathrm{X}^- \tag{37}$$

$$\mathrm{C} + \delta\mathrm{e}^- \rightleftharpoons \mathrm{C}^{\delta-} \tag{38}$$

Both reactions proceed simultaneously, since the overpotential for carbonization (37) is higher (by ∼1 V)[22,40] than the overpotential for n-doping (38). Cyclic voltammetry confirms reversibility of the reaction (38), although the charge recovery upon anodic oxidation is not perfect (40−94%).[25,40] The n-doping of electrochemical carbon can also be compensated by mild reductants, e.g., I_2.[201−203,258,269,270]

n-Doping by overreduction was observed during the carbonization of PTFE at Pt cathode (δ in the range of 0.05−0.45)[22,23,25] and by alkali metal amalgams.[51−53,271] In the latter case, well-reproducible doping levels (δ in the range of 0.20−0.21) were found, independent of the alkali metal type (Li, Na, K), reaction temperature (25−100 °C), and time.[53,271] The extra negative charge (δ^-) is compensated by electrolyte cations (M^+); hence the formal composition of the product is $CM_\delta(MF)_2$.

The n-doping rate of electrochemical carbon from hexachlorobuta-1,3-diene[38,39,41,128] increases, as expected, with decreasing size of M^+ (NBu_4^+, NEt_4^+, NMe_4^+).[40] n-Doping was also observed during electrochemical carbonization of PCTFE ($\delta = 0.32$),[53] Nafion 117 ($\delta = 0.20$),[46] PTFE−PPVE ($\delta = 0.21$),[53] FEP ($\delta = 0.2$),[66] C_6F_6 and C_6F_{14} ($\delta \approx 0.07-0.25$),[47] diiodoacetylene,[34,35] and PVDF ($\delta \approx 0.15$).[33]

Some authors[22,25,28,40] have regarded the interaction between the inserted cations M^+ and $C^{\delta-}$ as an intercalation into the graphite lattice. However, the potential at which the electrocarbonization[37,38] takes place (∼−2 V vs SHE) is too high to promote intercalation into graphite at $\delta \approx 0.2$.[22,271] A hypothetic graphite intercalation compound, e.g., $CM_{0.2}$, would have a sufficiently negative potential to drive a subsequent carbonization[22] of the precursor, e.g., PTFE:

$$CM_{0.2} + x(-CF_2-) \rightarrow x(-C-) + 2xMF + CM_{0.2-2x} \quad (39)$$

This was not observed: the doping level at the $CM_{0.2}$/PTFE junction remained unchanged even after years of contact.[53] Second, there is an apparent lack of graphite ordering in most electrochemical carbons (cf. section VI). A third argument against intercalation is the absence of H_2 in the hydrolysis products of CM_δ.[271] Hydrolysis yields, quantitatively, MOH and the corresponding "hydrocarbon", CH_δ:[271,272]

$$CM_\delta + \delta H_2O \rightarrow \delta MOH + CH_\delta \quad (40)$$

Therefore, the redox potential of CM_δ/C (cf. eq 38) must be even more positive than that of H_2/H^+ in alkaline medium (~−0.8 V vs SHE).[271] An organometallic species similar to carbides was also considered,[271] but the $C^{\delta-}\cdots M^+$ bond is most probably ionic and similar to that in n-doped polyacenic materials.[53]

B. Chemical Reactions

Electrochemical carbon is chemically very reactive. This manifests itself even in the absence of any external reactants by spontaneous cross-linking of polyyne-like chains (section VI). Oxidation with O_2 (air) proceeds readily at the room temperature to give surface oxides of varying composition,[65,177,244,272–274] which can further be modified by $SOCl_2$ and $ClSi(CH_3)_3$.[244] The reactivity of electrochemical carbon is useful in preparation of chemically modified electrodes[275] and chromatographic adsorbents.[244]

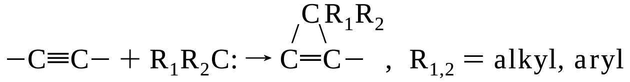
Most chemical studies were carried out with carbons originating from the fluoropolymer/M(Hg) reaction. The primary product is virtually stable, since the reactive carbon skeleton is preserved inside a compact composite (C−MF). This conservation packing disintegrates by extraction of MF with water,[272] $BF_3\cdot MeCN$,[276] $BF_3\cdot Et_2O$[201,202,276] and cyclic polyethers[201] in acetonitrile or tetrahydrofuran. However, hydrolysis (solvolysis) (cf. eq 40) is a complicating side reaction. A more clean way is to "open" the C−MF structure by recrystallization at ~300 °C in the presence of gaseous reactants (Br_2, S_8).[277,278]

Fixation of Br_2 at PTFE reduced by Li amalgam,[278] K/NH_3,[178] or benzoin dianion[64] indicates unsaturated links, but oxidative substitution is also at play:[278]

$$CM_\delta + \delta Br_2 \rightarrow CBr_\delta + \delta MBr \quad (41)$$

The halogen-modified carbons are precursors for subsequent modifications employing $NaPb(Et)_3$,[279] Grignard reagents,[244] and NH_3.[64] A direct fixation of NH_3 and NO was also described.[280]

Sulfur is, reportedly, added to unsaturated carbon chains to form reversibly reducible[281–283] heterocycles. However, cross-linking of chains by sulfide bridges and formation of surface sulfonates was also found.[277,280] A more selective reaction of unsaturated (triple bonded) chains in electrochemical carbon seems to be the addition of in situ generated carbenes:[276]



$$-C\equiv C- + R_1R_2C: \rightarrow \overset{CR_1R_2}{\overset{/\ \backslash}{C=C}}- \;,\; R_{1,2} = \text{alkyl, aryl} \quad (42)$$

Grafting of Fe(II) pyridine complexes,[275,284] alcohols,[201,202,234,275] butane sultone (4-hydroxy-1-butanesulfonic acid δ-sultone),[234] and ICN[201,202] was reported as well. A common problem of these reactions is that chemisorption and physical adsorption of the reactants and/or their followup products can hardly be distinguished.

V. Physical Properties of Electrochemical Carbon

A. Electrical and Magnetic Properties

The electrical conductivity of electrochemical carbons is primarily controlled by the level of doping. The conductivity of undoped carbon from hexachlorobuta-1,3-diene (10^{-6}−10^{-7} S/cm) increases to 4×10^{-4} S/cm upon electrochemical reductive or oxidative doping.[40] Analogously, carbons prepared by reduction of fluoropolymers with naphthalenide[203,285] and benzoin[270] radical anions or by dehydrohalogenation of PVDF[33,251,258] show conductivities of about 10^{-4}−10^{-5},[203,285] $<10^{-10}$,[270] or 10^{-11}−10^{-8} [33,258] S/cm. (In the latter case, the highest conductivity was found for electrochemically prepared material, which is naturally n-doped.[33]) Exposure to I_2 vapor causes first compensation effects (with n-doped materials)[33] and subsequent p-doping, accompanied by a dramatic conductivity increase, up to 0.3−40 S/cm.[270] n-Doping with naphthalenide[225,270] sometimes also increased the conductivity (up to 4.8×10^{-2} S/cm).[225]

The temperature dependence for I_2-doped carbons:[147,203,270]

$$\log \sigma_e = A - BT^{-1/4} \quad (43)$$

(A and B are constants) points to the Mott's variable-range electron hopping. The model is also valid for the as-received carbons made by PTFE/amalgam reaction.[57] It allows the estimation of the size of clusters among which the electron hopping occurs. The sizes determined for C−LiF (1.1−1.8 nm) are in reasonable accord with those obtained from X-ray diffraction.[57]

Cathodic reduction of halogenated hydrocarbons yields naturally n-doped carbons (cf. section IV.A); i.e., they already show high conductivities in the as-prepared state.[22,23,25,34,35,46,54,57] For instance, the ex-PTFE carbons have conductivities of 4.8 [22,23] or 10−100 S/cm,[25] but they decrease rapidly to 10^{-6}−10^{-8} S/cm levels after contact with air, methanol, or water.[22,23,25] A slower conductivity drop also occurred in nitrogen or vacuum, which was attributed to "disintercalation" of the n-doped carbon by the supporting PTFE (eq 39). Although the oxidative undoping leads to a conductivity of 1.4×10^{-4} S/cm,[22] this interpretation is presumably incorrect (see also section IV.A). Similar carbons made by PTFE/M(Hg) reaction showed no "disintercalation", but an opposite

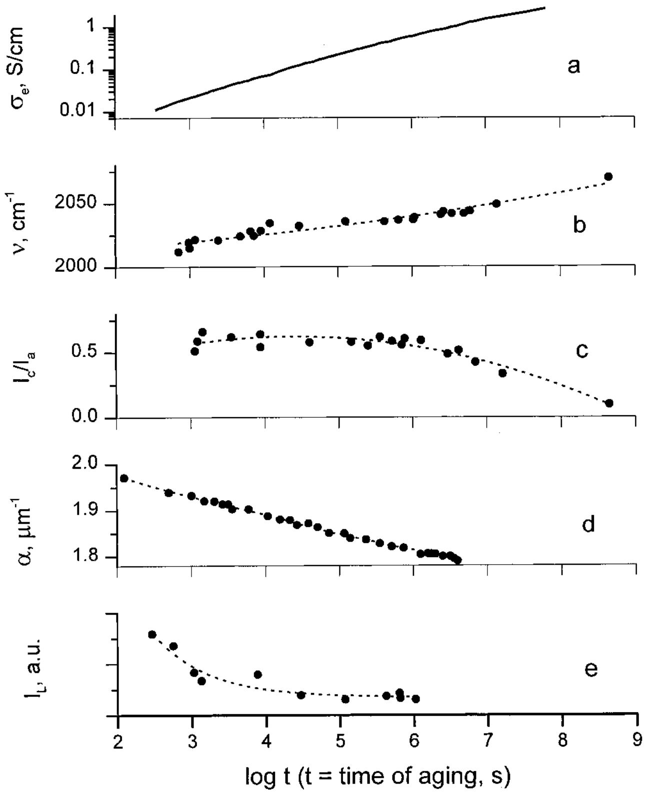


Figure 5. Aging effects in C−LiF prepared by the reaction of PTFE with Li amalgam at 25 °C. The sample was stored in vacuum at room temperature. σ_e is the electronic conductivity, ν is the wavenumber of the Raman band of the C≡C stretching vibration (excitation wavelength λ = 457 nm), I_c/I_a is the Raman intensity ratio of the C≡C line to that of the sp^2 carbon, α is the optical absorption coefficient at λ = 500 nm, and I_L is the intensity of photoluminescence at λ = 4.35 µm (excitation wavelength λ = 457 nm). Adapted from refs 44, 45, 54, 57, 306, and 310 and updated with recent data. Reproduced with permission from ref 310. Copyright 1994 Elsevier Science Ltd.

conductivity−time behavior, i.e., a spontaneous conductivity increase upon aging in vacuum.

This very unusual effect was first reported for C−LiF made from Nafion 117 and Li amalgam[46] and further studied in detail on C−MF (M = Li, Na, K) from PTFE and PCTFE.[54,56,57] Figure 5a shows the conductivity increase in a thin C−LiF layer on top of PTFE. For thin C−MF layers and aging times (t) substantially higher than the preparation time (t_0), the electronic conductivity scales with time:

$$\sigma_e = ct^{\epsilon} \qquad (44)$$

(c and ϵ are constants for the given alkali metal M.) The exponent ϵ equals 0.42, 0.15, and 0.02 for Li, Na, and K, respectively; i.e., the conductivity growth slows down with increasing size of the alkali metal cation. However, after long aging, the σ_e values are not much dependent on M ($\sigma_e \approx$ 1−5 S/cm at $t = 10^6$ s for Li, Na, and K).[54,57] For thicker C−MF layers, the age distribution in the direction normal to the sample surface cannot be neglected, which leads to a more complex equation:[56,57]

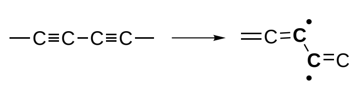
$$t_0^{\epsilon+1/2}\int_0^{\arcsin\xi}\cos^{2\epsilon+1}\phi \, d\phi = \sigma_e K_e \xi^{2\epsilon+1} \qquad (45)$$

where $\xi = (t_0/t)^{1/2}$ and K_e is a constant. This model predicts anisotropy in conductivity aging, i.e., the time independence of conductivities normal to the surface for $t \le t_0$. The doping/undoping effects were demonstrated by transient charge injection from the amalgam into "old" C−MF layers.[57] Compensation of n-doping by I_2 was also reported; stronger oxidants (O_2, Br_2) cause, however, irreversible effects.[269]

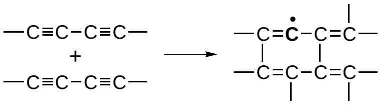
Electrochemical reductive carbonization of perhalogenated hydrocarbons requires that the product (C−MX composite) shows both electron (σ_e) and ion (σ_i) conductivities; the total conductivity is a series combination of σ_e and σ_i (cf. section I.B). Whereas σ_e values are easily accessible experimentally,[54,57] the ionic conductivities have been estimated only indirectly from kinetic data[53] (eq 7). For instance, the σ_i values found for the PTFE/M(Hg) reaction are (in S/cm, at 25 °C) 1.3 × 10^{-7}, 4 × 10^{-10}, and 5.7 × 10^{-13} for M = Li, Na, and K, respectively.[53] Apparently, the cation transport through the carbonized layer is the rate-determining process in the carbonization.

Ionic conductivities, σ_i, show an Arrhenius-like temperature behavior with roughly constant activation energies for ion transport (48−51 kJ/mol).[53] The σ_i values are significantly higher than the M$^+$ conductivities of solid alkali metal fluorides at the same temperatures. (They even vary differently with M for MF and C−MF). Hence, the M$^+$ cations are not conducted through the salt, MF, but through the n-doped carbon component (CM$_\delta$). Mechanistic details are unknown, but reversible association/dissociation cycles[31,32,245] (cf. eq 34) may play a role.

Magnetic properties of carbons provide important information about novel forms of carbon crystals.[286] Electrochemical carbon is paramagnetic, as evidenced by EPR of carbons made from PTFE by direct reduction at a cathode,[29] with naphthalenide,[234,287] benzoin dianion,[64] and Li amalgam.[272,288] In the latter case, the concentration of unpaired electrons in C−LiF ((3.2 ± 0.2) × 10^{18} spin/g, i.e., 2900 C atoms/spin) was reasonably reproducible, even after extraction of LiF from the composite. The creation of free radicals was attributed to kinking (46) or cross-linking (47) of sp-carbon chains, which are assumed to be primary reduction products of PTFE (see section VI):[289]



$$\text{—C≡C–C≡C—} \longrightarrow \text{=C=}\dot{\text{C}}\text{—}\dot{\text{C}}\text{=C=} \qquad (46)$$



$$\begin{array}{c}\text{—C≡C–C≡C—}\\ + \\ \text{—C≡C–C≡C—}\end{array} \longrightarrow \begin{array}{c}\text{—C=}\dot{\text{C}}\text{–C=C—}\\ \text{—C=C–C=C—}\end{array} \qquad (47)$$

Adsorption of diamagnetic molecules (NH_3) has little effect on the EPR spectra, but paramagnetic ones (NO, O_2, S_2)[272,280] cause reversible line broadening. This is pronounced for thin C−LiF layers (0.2−3 µm) or extracted pure carbons, but thicker C−LiF layers are less sensitive. This confirms the close packing of the C−LiF structure.

^{13}C NMR spectra of PTFE reduced by naphthalenide[234] and benzoin dianion[64] were also studied. In the latter case, the spectrum shows three resolved peaks of sp^3 (29.87 ppm), sp^2 (130.36 ppm), and sp

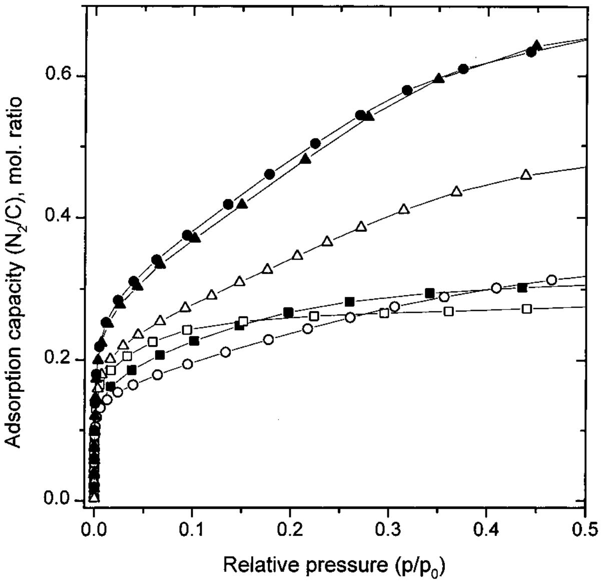


Figure 6. Adsorption isotherms of nitrogen at 77.2 K on electrochemical carbons. Samples were prepared by the extraction of the salt, MF from C−MF; the starting composite was obtained by the reaction of M-amalgam with PTFE (unless stated otherwise). (●) C−NaF washed with water, (▲) C−NaF washed with $BF_3{\cdot}(C_2H_5)_2O$ in acetonitrile, (△) C−LiF washed with $BF_3{\cdot}(C_2H_5)_2O$ in acetonitrile, (○) C−LiF processed by melting out LiF at 950 °C, (■) C−LiF washed with water, and (□) C−LiF (from hexafluorobenzene) washed with water. Reproduced from ref 291. Copyright 1995 ACS.

(80.70 ppm) carbons. Also, dehydrochlorination of PVDC yields a product with triple bonded (sp) carbon: 88.3 [252] or 66.8 ppm.[290]

B. Adsorption Properties

The BET surface area (from N_2 adsorption) increases by 4 orders of magnitude upon reduction of PTFE with Na/NH_3.[178] Analogously, the found double-layer capacitance of carbon made by a direct cathodic reduction of PTFE (~10 $\mu F/cm^2$) translates into a surface area of ~1000 m^2/g.[24,25]

As mentioned in section V.A, the high adsorption capacity of C−MF (made by the PTFE/M(Hg) reaction) appears only after the extraction of the salt, MF from the composite. Figure 6 displays some examples of nitrogen adsorption isotherms. Adsorption of N_2, Ar, benzene, and H_2O on the water-extracted C−LiF has been studied in detail.[291−298] The determined surface areas vary, depending on the adsorbate and the evaluation method used, from 1080 (benzene, DS method)[296] to 2940 m^2/g (N_2, BET method).[292] Extreme values, 3439−4150 m^2/g, reported by one group[293] are presumably incorrect (vide infra).[294]

This carbon material is a unique adsorbent with near-critical micropore volume and unusually large, sharply distributed micropores (“supermicropores”) of the radii of 1.2−1.4,[296] 0.75−0.9,[292] or 0.96 nm[294] but negligible proportion of meso-,[296] macro-,[292] and ultramicropores.[291] Small-angle X-ray scattering revealed a comparable pore radius (0.85 nm).[299] The supermicroporous texture of electrochemical carbons makes the assessment of true surface areas problematic for principal reasons.[291] Empirical analysis (α_s plot) yields values between 1070 and 1680 m^2/g for the samples of Figure 6.[291]

Carbons extracted from C−LiF by $BF_3{\cdot}Et_2O$ have a significantly larger adsorption capacity than those prepared in aqueous medium; extreme values were found for carbons from C−NaF (Figure 6).[291] The best materials exhibit adsorption of >0.3 N_2 molecules/carbon atom at relative nitrogen pressures of $p/p_0 \gtrsim 0.05$ (p_0 is the N_2 vapor pressure at −196 °C). Theoretically, a N_2 monolayer on a single graphite plane (graphene), covered on both sides, corresponds to 0.32 N_2/C.[291] This value is considered usually as a natural adsorption limit of elemental carbon. However, if we suppose a monolayer process also in the supermicropore filling, adsorption capacities exceeding that of graphene are theoretically possible.[300]

Electrochemical carbons were also tested as adsorbents in gas[301,302] and liquid[244,298,303,304] chromatography. Adsorption of hydrocarbons,[244,298,302] alcohols,[298,302] chlorinated hydrocarbons,[298] amino acids,[298] CO_2, H_2S, and SO_2,[301] and carboranes[303,304] was studied. In the latter case, excellent resolution of carborane isomers in HPLC was observed.[303,304]

C. Optical Properties, Spectroscopy

UV−visible spectra of electrochemical carbon from hexachlorobuta-1,4-diene,[39] PTFE reduced by benzoin dianion,[64,224] dehydrohalogenated PVDF,[207,251,258,305] PVDC,[252] chlorinated polyacetylene,[263] and poly(vinyl chloride)[266] show a broad absorption maximum near 2−4 eV, which qualitatively points at a complicated π-conjugated carbon network.

Thin C−MF (M = Li, Na, K) films made by the reaction of PTFE[306] or FEP[44,60,269] with M(Hg) show analogous absorption maximums at 3−4.5 eV. It is red-shifted upon aging at room temperature, while the optical densities change with an isosbestic point at ~2 eV (bleaching in the red region and vice versa). These effects are controlled by a defined kinetics, analogously to the time changes of electronic conductivity (section V.A). The decrease of optical absorption coefficient (α) in C−LiF at λ = 500 nm is demonstrated in Figure 5d. Also, the intensity of photoluminescence (I_L) decays on a comparable time scale upon aging (Figure 5e).[44]

A model of the absorbance−time behavior cannot neglect the fast chemical initialization (eq 8), since for thin films, L_0 and L_1 are comparable (cf. section I.B). The solution leads to relative time changes of the absorbance maximum, A/A_0:[60]

$$\frac{A}{A_0} = \xi^{2\beta}\,\frac{\xi^{-1}\,\psi(\xi,\beta) + \Delta L}{\psi(1,\beta) + \Delta L} \tag{48}$$

where $\xi = (t_0/t)^{1/2}$ (as in eq 45). A_0 denotes the initial absorbance of a freshly grown C−MF layer and

$$\psi(\xi,\beta) = \int_0^{\arcsin\xi} \cos^{1-2\beta}\omega \; d\omega, \quad \Delta L = L_1/(L_0 - L_1) \tag{49}$$

The exponent β depends on M: 0.0061 (C−LiF), 0.0049 (C−NaF), and 0.0033 (C−KF), which resembles the same trend in electronic conductivities (section V.A; eqs 44 and 45). UV−visible spectra

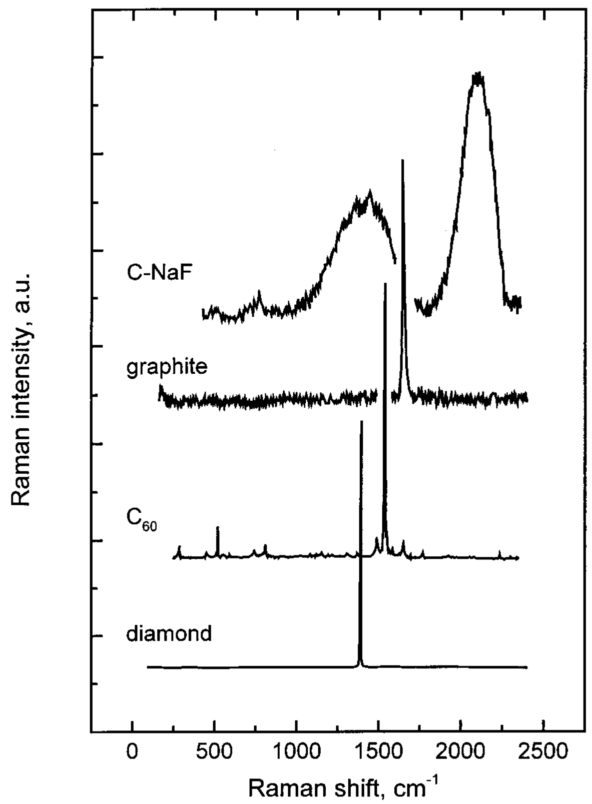


Figure 7. Raman spectrum of C−NaF prepared by the reaction of PTFE with Na amalgam at 25 °C. For comparison, spectra of the three common allotropic modifications of elemental carbon (hexagonal graphite, fullerene C_{60}, cubic diamond) are displayed. Excitation wavelength λ = 457 nm. Unlike C−NaF, the reference samples are single crystals. Reproduced with permission from ref 310. Copyright 1994 Elsevier Science Ltd.

support the theoretically expected[307,308] transition from a semiconductor to metal-like band structure, if the carbon (polyyne) chains are cross-linked (cf. section VI).

Infrared spectra of various carbons derived from PTFE,[29,64,65,191,205,225,234,272] PCTFE,[207,281] FEP,[65] hexachlorobuta-1,3-diene,[38,39] CCl_4,[42] diiodoacetylene,[34,35] C_6F_6, and C_6F_{14}[47] usually indicate a complicated mixture of surface oxides (−OH, =O, −COOH, and combinations), created by air exposure during the sample preparation and/or measurement. Incomplete carbonization, impurities (adsorbed solvents), and n-doping (NR_4^+ insertion) are also detectable.[34,35,39,42,64,65,225] Alternatively, surface oxides and impurities are observed by XPS.[46,47,65,177,179,205−207,209,244,257,273] Problems with impurities and incomplete carbonization are avoided in the Raman spectra of C−MF (M = Li, Na, K), studied in situ by Kuzmany et al.[44,45,309]

The spectral assignment in the region of the carbon skeleton is difficult, except for the characteristic C≡C stretching vibration[29,34,35,64,65,225] at 2000−2200 cm^{-1}. It appears also in the Raman spectra of carbons from PTFE,[44,45,64,225,309,310] diiodoacetylene,[34,35] and perfluoro-*n*-alkanes.[45] Figure 7 displays a comparison of the Raman spectra of C-NaF (polycrystalline) with those of the common carbon allotropes (single crystals). Carbons made by dehydrohalogenation of poly(vinylidene halides),[33,239,250−254,311,312] poly(trichlorobutadiene),[257] chlorinated polyacetylene,[263] and poly(vinyl chloride)[266] also show the IR[33,239,250−254,257,263,312] and Raman[252,263,266,311] active C≡C stretch. A weak (uninterpreted) band at ~2200 cm^{-1} appears in SERS of ethylenediamine-derived carbon.[75] On the other hand, this band is missing in the spectra of carbons from CCl_4,[42] hexafluorobenzene,[45] CO_2, and formate,[75,80,81] which all show the graphite-like vibrations only. Electrochemical carbons from hexachlorobuta-1,3-diene also show only graphite-like Raman spectra,[38,39] but other authors[11,36,37] have reported the C≡C stretch at 1950 cm^{-1}.

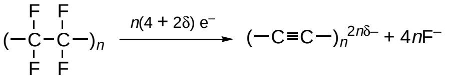
Raman spectra of C−MF were studied in detail at varying excitation wavelengths (resonance enhancement), time of aging,[44,310] type of M,[44] and type of perfluorinated precursor,[45] and the data were interpreted in terms of the conjugation length model of oligoynes.[44,309,313,314] The intensity of the C≡C line relative to that of sp^2 carbon in C−KF (from PTFE) equals $I_c/I_a = 2.2 \pm 0.2$ at $\lambda_{exc} = 457$ nm.[44,45] There exists no other solid carbon material showing such intense Raman signal of triple-bonded carbon.[44,45,309,310] A monotonous upshift of the frequency (Figure 5b) and downshift of the intensity (Figure 5c) of the C≡C line with time of aging proceed in parallel with the above-mentioned time changes of UV−visible absorption (Figure 5d), photoluminescence (Figure 5e), and electronic conductivity (Figure 5a).[44,309,310] They are normally slow (years) but accelerate upon heating and especially after extraction of MF from the composite.[45]

VI. Structure of Electrochemical Carbon

Carbons prepared in organic electrolyte solutions or similar media usually show variable composition owing to incomplete carbonization and side reactions with solvents and impurities. Hence, plausible structural assessments appear only for the best defined materials, such as carbons made from perhalogenated hydrocarbons and alkali metal amalgams. Strictly speaking, they are not elemental carbons either, but n-doped elemental carbons with interspersed alkali metal halide (section IV.A).

A. C−MF and Related Materials

A product of the PTFE/M(Hg) reaction (C−MF, M = Li, Na, K) permits most consistent structural conclusions to be reached. It is believed that this reaction primarily gives n-doped polyyne:[44,45,269,289,309,310]



$$(-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-)_n \xrightarrow{n(4+2\delta)\,e^-} (-C{\equiv}C-)_n^{2n\delta-} + 4nF^- \qquad (50)$$

Ab initio Hartree−Fock calculations of infinite carbon chains confirm that polyyne (polyethynylene) is favored energetically over the isomeric polycumulene (poly(ethylenediylidene)),[315−318] $(=C=C=)_n$.

Polycumulene converts to polyyne through a Peierls distortion; the calculated Peierls gaps are in the range of 2−5 eV,[319−321] and the bond lengths were predicted to be 113.0 and 132.1 pm[318] or 122.9 and 138.7 pm.[322] Other theoretical studies of polyyne supplied data about doping,[320,322,323] electron correla-

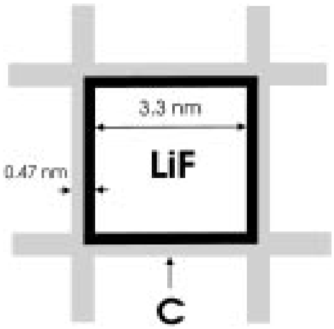


Figure 8. Scheme of the nanosized texture of the C−LiF composite. The pattern follows from the LiF crystal size determined by X-ray diffraction[54,299] and the experimental densities of the C−LiF composite (2.24 g/cm^3) and LiF (2.652 g/cm^3).[289] The space between cubes is filled with carbon; the corresponding theoretical density in this space equals 1.4 g/cm^3. Reproduced with permission from ref 289. Copyright 1980 Elsevier Science Ltd.

tion,[324] reaction with sulfur,[321] nonlinear optical properties,[325−327] excited states, and chain defects (polarons, excitons, twistons).[320,328−330]

However, both theoretical calculations[307,308] and experimental experience show that polyyne is unstable against kinking and cross-linking (eqs 46 and 47), which results, eventually, in the formation of graphene.[331,332] In C−MF composites, the polyyne-to-graphene conversion is blocked sterically by interspersed nanocrystalline salt (crystal size of ∼3.3 nm for LiF, cf. Figure 8),[289,299,333] which causes polyyne to be detectable even after 14 years of aging in vacuum at room temperature.[45]

This picture is supported by the X-ray diffraction analysis of C−LiF (from PTFE).[334,335] It gives the average carbon−carbon distance of (135 ± 4) pm,[335] interpreted as a superposition of graphitic (142 pm, 70−45%), diamond-like (154 pm, 0−15%), and polyyne (∼120 pm, 30−40%) structures. Extended graphitic ordering is excluded already by a simple comparison of crystal sizes and densities of individual components in C−LiF: it shows that carbon lamellae thicker than 470 pm (about two graphite layers) cannot occur in a monodisperse composite (Figure 8).[289,333] The carbon network in Figure 8 exhibits theoretically a surface area of 3039 m^2/g (cf. the discussion of adsorption isotherms in section V.B).

The structural model of polyyne/graphene has been further upgraded on the basis of Raman spectroscopy. The yield of polyyne in C−MF increases and the cross-linking rate decreases with the molar volume of MF (Li < Na < K).[44] As expected, the spatial separation of polyyne chains is crucial for their stabilization. The Raman frequency of the Σ_g mode of oligoynes scales with the number of C≡C bonds.[44] The increase of conjugation lengths in the series Li < Na < K is again apparent: C−KF exhibits ∼14 carbon atoms in polyyne conjugation.[44] An even higher value was found in carbons from stretch-oriented PTFE: polarization measurements indicate 16-member polyyne chains, oriented in the direction of stretching.[45] This conjugation length is among the largest deducible from Raman spectra of polyyne-like solid carbons ("carbynes");[34−37,252,263,266,311,336−339] there is only one report about a 20-member polyyne chain in electrochemical "carbyne" from hexachlorobuta-1,3-diene.[36] The sometimes reported large conjugation lengths[263,266] (up to 130 C atoms)[263] are incorrect in view of the refined conjugation length model by Kuzmany et al.[44,309]

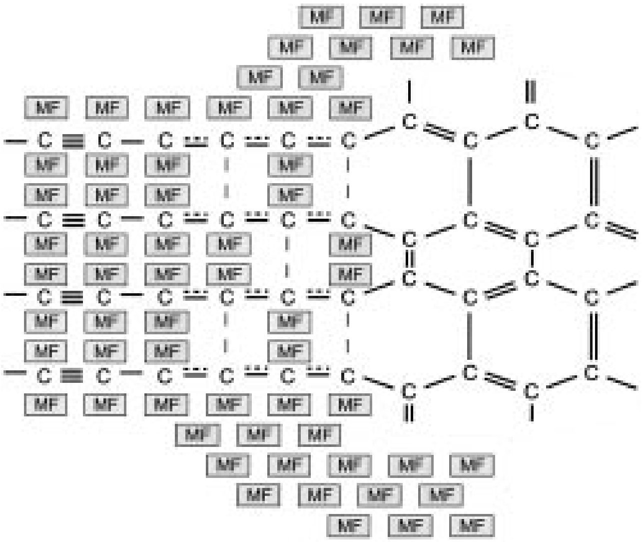


Figure 9. Scheme of structural changes in C−MF composite (from PTFE) upon aging.

The polyyne decomposition is accompanied by regular changes of the electronic conductivity, UV−visible and Raman spectra and photoluminescence (cf. Figure 5), and the MF crystallite size,[54] which is interpreted in terms of polyyne cross-linking. Hence, the comparison of polyyne yields and stabilities for various M leads to a self-consistent structural picture. Figure 9 shows schematically the structural changes during the C−MF aging. The left-hand side of Figure 9 corresponds to a freshly prepared composite with a large proportion of sp-bonded carbon moieties; the right-hand side is "old" cross-linked material.

Polyynes are also formed (as in reaction 50) from other chainlike perhalogenated precursors, both polymers[11,31,33,45,246] and small molecules,[11,12,34−37,45,47] although the yields are generally lower than those from PTFE.[45] Hexafluorobenzene does not give any polyyne, but graphite-like carbon only, because the electrochemical splitting of C−C bonds is excluded.[45] Graphite-like structures also result from other precursors that do not possess linear chains (CCl$_4$,[42] CO$_2$ and formate[75,80,81]).

The structure of pure carbons made by extraction of the salt from C−MF, was subjected to theoretical modeling[340] and experimental investigations. The carbon grains possess lamellar morphology with particle size of 12 ± 9 (from electron microscopy)[299] or 4−10 μm (from sedimentation analysis).[303] The polyyne skeleton collapses rapidly upon removal of MF,[45] while the product contains only sp^2 and sp^3 carbon atoms (75/25 ratio).[334,335] X-ray diffraction and electron microscopy displayed nodular carbon clusters, ∼1.1−1.2 nm in size,[299,334,335] with a chain-like ordering, similar to that in PTFE.[299] Upon heating, the clusters grow to 2.4−3.2 nm, without pronounced change in the sp^2/sp^3 ratio.[334,335]

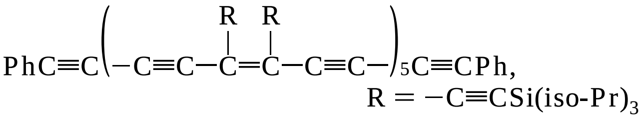
B. Some Aspects of the Existence of (Electrochemical) Carbyne

In this chapter, the name “carbyne” will denote a hypothetical carbon allotrope, containing sp-bonded carbon atoms.[87,341−343] Presumably, pure carbyne was never obtained, although there are continuing reports on its synthesis,[34,35,84,250,344−353] as well as natural occurrence.[354−357] Convincing evidence, such as complete X-ray structure, is missing. This makes the problem of carbynes one of the most confusing topics in carbon science (for reviews, see refs 87, 88, 310, 342, 343, and 357−361).

The only defined species approaching carbyne are end-capped oligoynes and similar carbon-rich molecules which are accessible through advanced acetylene chemistry:[86,362−364]

$$\mathrm{Et_3Si(-C{\equiv}C-)_{16}SiEt_3}$$

or



$$\mathrm{PhC{\equiv}C\left(-C{\equiv}C-\overset{R}{C}{=}\overset{R}{C}-C{\equiv}C-\right)_5C{\equiv}CPh,}\quad \mathrm{R = -C{\equiv}CSi(iso\text{-}Pr)_3}$$

The latter example displays a carbon rod, 4.92 nm in length). These molecules exhibit facile electrochemical reduction,[365] which resembles the n-doping of electrochemical carbon (cf. section IV.A). Another example is metal-capped oligoyne:[366−368]

$$\mathrm{Re^*(-C{\equiv}C-)_{\mathit{x}}Re^*;}\quad x = 2-10,\ \mathrm{Re^* = (\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)}$$

These species are also electrochemically active: they show a reversible one-electron oxidation (predominantly metal-centered) but no reductions up to −1 V.[367,369] Still other examples are end-capped polyynes, produced by quenching of the carbon vapor with $^\bullet CF_3$ or $^\bullet CN$ radicals; they reportedly contain chains of up to 300 carbon atoms and are surprisingly stable and soluble in organic solvents.[347] Shorter end-capped oligoynes even occur naturally in certain biological objects (fungi, tropical weeds)[370−373] and in the cosmos (interstellar clouds, cool carbon stars).[374,375]

A further class of more or less defined species approaching carbyne are all-carbon molecules occurring in the carbon melt,[376] vapor or in inert matrixes at low temperatures:[377−379]

$$\mathrm{^\bullet C(-C{\equiv}C-)_{\mathit{n}}C^\bullet}\qquad \text{or}\qquad \mathrm{{:}C{=}(C{=}C)_{\mathit{n}}{=}C{:}}$$

An “infinite” polyyne chain has theoretical significance only,[315−330,380,381] but polymeric all-carbon networks containing sp-bonded links together with the “usual” (sp^2, sp^3) structures may be stable enough to be realized synthetically. These predicted networks include graphynes,[382,383] fullereneynes,[384,385] “superdiamond”, and many others.[86,363,386−389]

An sp-bonded chain is not perfectly linear (already in model oligoynes[347,390]), which leads to a speculation that long chains possess a helical conformation.[347] Also macrocyclic polyynes, such as C_{18} [391] are quite realistic.[86,363,392] (They are, for example, the probable precursors in the formation of fullerenes[393,394] and nanotubes[395]). On the other hand, Heimann et al. have regarded a polyyne helix as unlikely in carbyne crystals.[396] They suggested a model of kinked polyyne/polycumulene[359,360,396] with impurity-stabilized kinks[312,360,397] and the linear chain segments running parallel to the hexagonal *c*-axis. This “pencils-in-box” model is also shared by some other groups.[312,348,349,397] Alternatively, the kinked sp-carbon chains may form an all-carbon crystal with regular allene[387] or polydiacetylene moieties.[388,389] (Strictly speaking, all these models disregard the original definition of carbyne as a purely sp-bonded carbon allotrope.) Carbyne was sometimes localized into the low-pressure region of the carbon *p*, *T*-phase diagram,[398] and carbynoid chains are predicted to be stable in carbon melt at ~5000 K and 1 g/cm^3.[376]

Decisive works on carbyne require a preparation of reasonably sized single crystals.[399] Among many physical and chemical attempts, the electrochemical carbonization[11,33−35,44,45,269,309,310] seems hopeful. Surprisingly good polyyne-like materials result from cathodic defluorination of PTFE.[44,45,309,310] Similar products were electrosynthesized from PVDF,[11,33] C_2I_2,[11,34,35] C_2H_2,[11,12] hexachlorobuta-1,3-diene,[11,36,37] and some other precursors[11,45] (for a review, see ref 11). A spontaneous natural n-doping may introduce impurity stabilization and defined spatial ordering of equally charged chains. This strategy gives better defined products than the alternative chemical ways of removing substituents from halogenated polymers. However, more work is needed to learn whether or not a new carbon allotrope is, eventually, accessible.

VII. Concluding Remarks

Electrochemical carbon is primarily a subject of academic interest, although there are links to practical outputs, such as fixation of CO_2,[17−19,95] electrochemical power sources,[20,43,234,281,282] chromatography,[244,298,301−304] sensors,[204,234,275,284] etc. Other reported applications refer to surface treatment of fluoropolymers for adhesive bonding,[183−187] metalizing,[209,212,214,217−219,226] antistatic modification,[194,401] and surgical[178] and electronic applications.[195] The preparation of electrochemical carbon from PTFE or PCTFE,[202,402−407] Nafion,[408] and low molecular weight perfluorinated molecules[409] is safeguarded by patents. Electrochemical carbons are excellent adsorbents, but compared to common active carbons, they are handicapped by high cost.

Electrochemical carbonization of organic precursors is a useful strategy in molecular engineering of all-carbon networks. Since the reaction occurs at mild conditions (without cracking of the C−C bonds), the structure of electrochemical carbons is considerably precursor-dependent. This allows the electrosynthesis of polyyne-like skeleton from a linear perhalogenated hydrocarbon[33−35,44,45,269,309,310] or graphite from an aromatic precursor.[45] Although no defined crystalline product has resulted yet, this is a challenge for future efforts: the fascinating structural variability of carbon compounds should also be reflected in structures of the carbon allotropes. The discovery of fullerenes is a confirmation of this idea.

VIII. Acknowledgments

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IX. References and Notes

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