Chapter 2
Paper

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Abstract Paper is a fibrous sheet material made from fibers based on a variety of materials: wood cellulose, synthetic polymers, mineral fibers (glass, basalt, and asbestos), and other material (wool, mica, metallic "whiskers," and graphite). The most common type of paper is writing paper. Its main feature is the capillary-porous structure that allows the absorption of inks, dyes, and graphite pencil powder. Paper (the Italian bambagia—cotton) is a fibrous sheet material. Paper with weight exceeding 250 g per m^2 is called cardboard. Distinguishing between general-purpose paper (mass and non-mass) and special, a decision was made to divide paper into a number of classes for printing (newsprint, offset, etc.), writing, typing, drawing and crayon, for paper money, for vehicles (punch-card, ticker-tape, etc.), electrical (cable, capacitor, etc.), wrapping and packaging, etc.

2.1 History

Paper is the most ancient of all humanity artificially made porous products. The Chinese Chronicle reported that paper was invented in 105 AD by Tsai Lun. However, in 1957, in the Baotsya Cave in northern China's Shansi Province, a tomb was discovered where scraps of paper sheets were found. The paper was investigated and it was found that it was made in the second century BC. Prior to Tsai Lun, paper in China was made from hemp, and before that from silk, which is made from defective silkworm cocoons. Tsai Lun pounded mulberry fibers, wood ash, cloth, and hemp. He mixed these with water and put the mass on the form (wooden frame and a screen of bamboo). After drying in the sun, he smoothed this mass with stones. The result was a solid sheet of paper. After the invention of Tsai Lun, the process of paper production began to improve rapidly. Starch, glue, natural dyes, etc., were added to enhance the strength of paper (Fig. 2.1).

At the beginning of the seventh century the papermaking method was known in Japan and Korea. And after 150 years, via prisoners of war it came to be known by the Arabs. In the sixth to eighth centuries, paper production was carried out in

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Fig. 2.1 Making paper by Tsai Lun

Central Asia, Korea, Japan, and other Asian countries. In the eleventh to twelfth centuries, paper appeared in Europe, where it replaced animal parchment. Starting from the fifteenth to sixteenth centuries, after the introduction of printing, paper production grew rapidly. Paper was manufactured in a very primitive way—manual milling of mass by wooden mallets in a mortar and scooping it by the forms with a mesh bottom. Of great importance in the development of paper production was the invention of the milling machine roll during the second half of the seventeenth century. At the end of the eighteenth century rolls were allowed to produce a large number of paper pulp, but handmade casting (scooping) delayed the growth of paper production.

In 1799, N.L. Robert (France) invented the paper machine, mechanized casting of paper through the use of an infinitely moving grid. In England, the brothers G. and S. Fourdrinier, buying the Roberts patent continued to work on the mechanization of casting, and in 1806 patented a paper machine. By the middle of the nineteenth century, the paper machine had turned into a sophisticated unit that could run continuously and largely automatically. In the twentieth century, paper production became a major and highly mechanized brunch of industry with a continuous-thread processing chain having powerful thermo-electrical stations and complex chemical manufactories for the production of fibrous half-stuffs.

2.2 Production

Nowadays, paper is made from fibrous semifinished: wood cellulose, wood pulp—a product of abrasion of timber; the so-called thermo-mechanical pulp obtained by mechanical grinding (milling) of steamed wood chips; semicellulose—the product of chemical and the subsequent machining of wood; fibers of cotton, flax, hemp, and jute. Paper wastes are widely used in the manufacture of paper. Special types of paper are made from synthetic polymers, mineral fibers (glass, basalt, and asbestos), and other materials (wool, mica, metal "whiskers," and graphite).

Manufacture of paper includes a series of sequential steps: preparing pulp, paper manufacture on the paper machine, its finish processing, handing out, and packaging. Preparation of pulp is reduced to grinding, preparation of the composition, and cleaning of mass. Grinding is mechano-chemical treatment of the fibrous semifinished in water, commonly using conical and disk mills of continuous action; thus, changing the shape and size of the fibers, their swelling occurs, thin fibers—fibrils are detached from the outer surface. The composition of pulp depends on the form of paper produced. Typically, paper contains several types of semi-finished fibers, mineral fillers, sizing agents, and excipients. Thus, the composition of newsprint paper comprises 70–85 % of wood pulp and 15–30 % of wood cellulose. Then, the resulting mass is diluted and subjected to so-called screening. As a result, clusters of fibers are removed, the fibers are uniformly dispersed in water preventing the formation of fiber associates (flocculation) and chaotic sequential interlacing of fibers is provided.

Papermaking involves feeding of an aqueous suspension (dispersion) containing 0.1–1.0 % of solids in a papermaking machine, casting of the paper web in the grid part of the machine on a moving continuous grid (one or several), its pressing, drying, calendering, and coiling. In the grid part of the machine most of the water runs off and a sheet of paper is formed and sealed, passing on the grid consistently over various dewatering (suction) elements of the machine. The removed water is mainly used for diluting the pulp. In the press section of a paper machine, a paper flat is wrung out using a special cloth by several pairs of nip rolls and compacted. In the drying chamber of the machine, a paper web is pressed against the surface of the steam-heated drying cylinders by a dryer cloth. Sometimes the paper is dried on an air cushion.

The chaotic intertwining of fibers, bundles of fibrils, and individual fibrils, which are pulled together during drying to form a strong interfiber and interfibrillar links is provided in the preparation of the suspension and its dehydration. Surface finishing of the paper is going on in contact with a smooth surface of drying cylinders. The smoothness of the paper is further increased by calendering. The resulting paper is wound into a roll, sometimes gets off to further increase the smoothness (super-calendering), and then cut into sheets or rolls of predetermined size. Sometimes, during the production of paper the air is used as a dispersion medium instead of water (so-called dry method). Much of the paper is subjected to further treatment and recycling. For example, in order to improve printability, paper is subjected to so-called chalking, which is the surface coating generally containing kaolin and binder (latex, modified starch, carboxymethyl cellulose, or the like). To obtain waterproof packing, the paper surface is coated with polyethylene film, for roofing and waterproofing soft paper materials the paper is impregnated with solutions of bitumen.

2.3 The Structure, Properties, and Applications

Paper is a composite material. In addition to various fibrous reinforcing components, which create a continuous matrix, the paper may contain mineral fillers, which impart its opacity and enhancing whiteness and smoothness; as well as colorants, polymeric binders, and others. Sizing agents (rosin-based adhesive, etc.) prevent the spread of ink and China ink on the surface of the carcass paper and penetration of inks to the opposite side of the sheet. Synthetic resins, lattices, and crosslinkers provide wet strength. Common types of paper have a capillary-porous structure and are composed of fibers, bundles of fibrils, and individual fibrils, linked by hydrogen bonds, van der Waals forces, and friction. These bonds are formed during paper drying in which a vitrification of the polymer components of papermaking fibers (cellulose, hemicellulose, and lignin) goes on under considerable shrinkage stresses, which constrict fibrillar elements of the paper structure.

Hemicellulose in the production of paper can partially pass into the viscous-flow state and become vitrified during drying. This structure causes hydrophilicity of most types of paper, reduction in strength when wetting, dependence of the properties and dimensions on the relative air humidity. On the grid of the Fourdrinier machine pulp fibers are oriented predominantly in the direction of movement to a greater extent at the bottom (grid) side of the sheet and to a lesser degree on the top (front) side. Therefore, the paper is anisotropic in all directions. Anisotropy is amplified by uneven thickness distribution of fine fibers, fillers, and sizing agents. Paper and paperboard produced by multi-grid machines, as well as coated paper, such as an enameled (chalk overlay) paper have for example a multilayer structure.

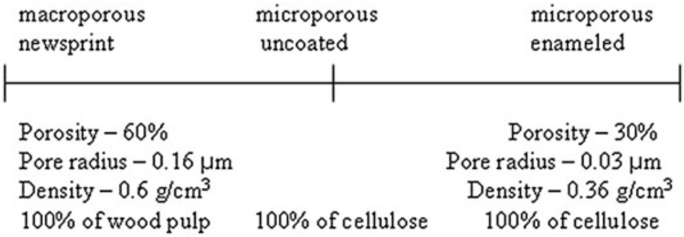
A bulk weight of paper ranges from 0.40 to 1.35 g/cm3, fracture resistance—from one to tens of thousands of double folds, specific heat capacity—from 1.21 to 1.32 kJ/(kg*K). Specific volume resistivity of insulating species of an absolutely dry paper is 10–100 ohm* m, the dielectric constant—2.2–5.0. Printing and writing paper perceive printing dye, ink, Indian ink, and pencil, and possess sufficient strength and durability (the latter requirement does not apply to a newsprint paper). Wrapping paper characterized by good physical and mechanical properties: high dynamic strength (sack paper), hardness (corrugated paperboard), etc. Paper filters having predetermined capillary pore structure and high rigidity are used for purification of gases and liquids, e.g., oils and fuels in internal combustion engines. Tissue paper (toilet, sanitary napkins, diapers, paper towels, and disposable underwear) has high absorbency with sufficient mechanical and wet strength. Paper used as a carrier of information in electronic computer engineering has high mechanical strength (punched tape), flatness (punched card), and dimensional stability. Paper used as a recording object in reproduction systems for the extraction of information has "functional" coating (light-and heat-sensitive, semi-conductor paper, etc.). Sticky paper with special coatings is used for mechanized packaging and labeling, and with anti-adhesive coatings—for packing sticky materials.

2.4 Porosity

Porosity directly affects the absorbency of paper, that is, its ability to receive the ink and may well serve to characterize the structure of paper. As already mentioned, paper is a capillary-porous material with the distinction of macro and microporosity. Macropores—the space between the fibers is filled with air and moisture. The micropores or capillaries are the smallest and irregularly shaped spaces penetrating the coating layer of chulk overlay papers, and also form between the filler particles or between them and the walls of the cellulose fibers in uncoated papers. Capillaries are presented also inside cellulosic fibers. All uncoated, not too compacted papers, such as newsprint, are macroporous. The total pore volume in such papers is as high as 60 % or more and the average pore radius is about 0.16–0.18 μm. These papers absorb ink well thanks to its loose structure, which is a highly developed inner surface. Coated papers are microporous or capillary structures. They also absorb ink well but by the forces of capillary pressure. Here, the porosity is only about 30 % with a pore size less than 0.03 μm. The rest of the paper is in an intermediate position. In fact, this means that printing on offset paper leads to penetration of solvents in paints and pigments as well into the pores. Thus, the concentration of pigments on the surface is small and therefore it is impossible to achieve saturated colors. When printing on a chalk overlay paper, the pore diameter of coated layer is so small that only the solvents are absorbed into the pores, while the pigment particles remain on the paper surface. Therefore, the image is very rich.

2.5 Sorption Properties of the Paper

Absorbency is one of the most important properties of printed paper. Proper assessment of absorbency means implementation of conditions of the timely and full consolidation of paint and as a result—getting a quality print. The absorbency of paper is primarily dependent on its structure, as the interactions of paper with ink are fundamentally different processes. Before talking about the features of these interactions in certain cases, it is necessary to recall once more the main types of structures of modern printing paper. If we represent the structure of paper in the form of a scale, a macroporous paper consisting entirely of wood pulp, such as newspaper, will accommodate at one of its ends. The other end of the scale, respectively, will be occupied by a purely microporous cellulosic paper such as enameled paper. A little to the left will house a purely microporous cellulosic uncoated paper. And all the others will take the remaining gap.



Macroporous paper is receptive to ink, absorbing it as a whole. Dyes here are low-viscous. Liquid dye quickly fills large pores, soaking in a large enough depth. Its excessive absorption can even cause “punching” of the impression, that is, the image becomes visible on the reverse side of the sheet. Improved macroporosity of a paper is undesirable, for example, in the case of an illustrative printing when excessive absorption results in a loss of saturation and gloss of paints. For microporous (capillary) papers, the mechanism of “selective absorption” is known as a characteristic one, when under the action of capillary pressure in the micropores of the surface layer of the paper, low viscous component of a dye (solvent) is absorbed predominantly and the pigment and film former remain on the paper surface. This is what is required to get a clear picture. Since the mechanism of the interaction between paper and dye in these cases is different, a variety of dyes is prepared for coated and uncoated papers.

2.6 Banknote Paper

Paper for the production of banknotes is a special, thin sheet material, consisting mainly of bonded with each other vegetable fibers. Taking into account the special characteristics of banknote paper, cotton, linen, and other fibers are used in its manufacture. Since banknotes are instruments of cash circulation, paper for them should have high resistance to wear. Banknotes must have high mechanical strength and resist repeated wrinkling, abrasion, and bending. Paper for banknotes should have good printing properties in order to receive and store the image, including the required optical properties of light color and opacity. It is also necessary to comply with certain characteristics of softness and smoothness. Very important properties are the light-fastness and durability as well as resistance to various physical and chemical influences—the necessary quality in the long process of banknotes circulation.

We applied the standard contact porosimetry method (SCPM) to study various samples of banknote paper. In Fig. 2.2 integral (a) and differential (b) porogramms which were measured using water (1) and octane (2) are presented.

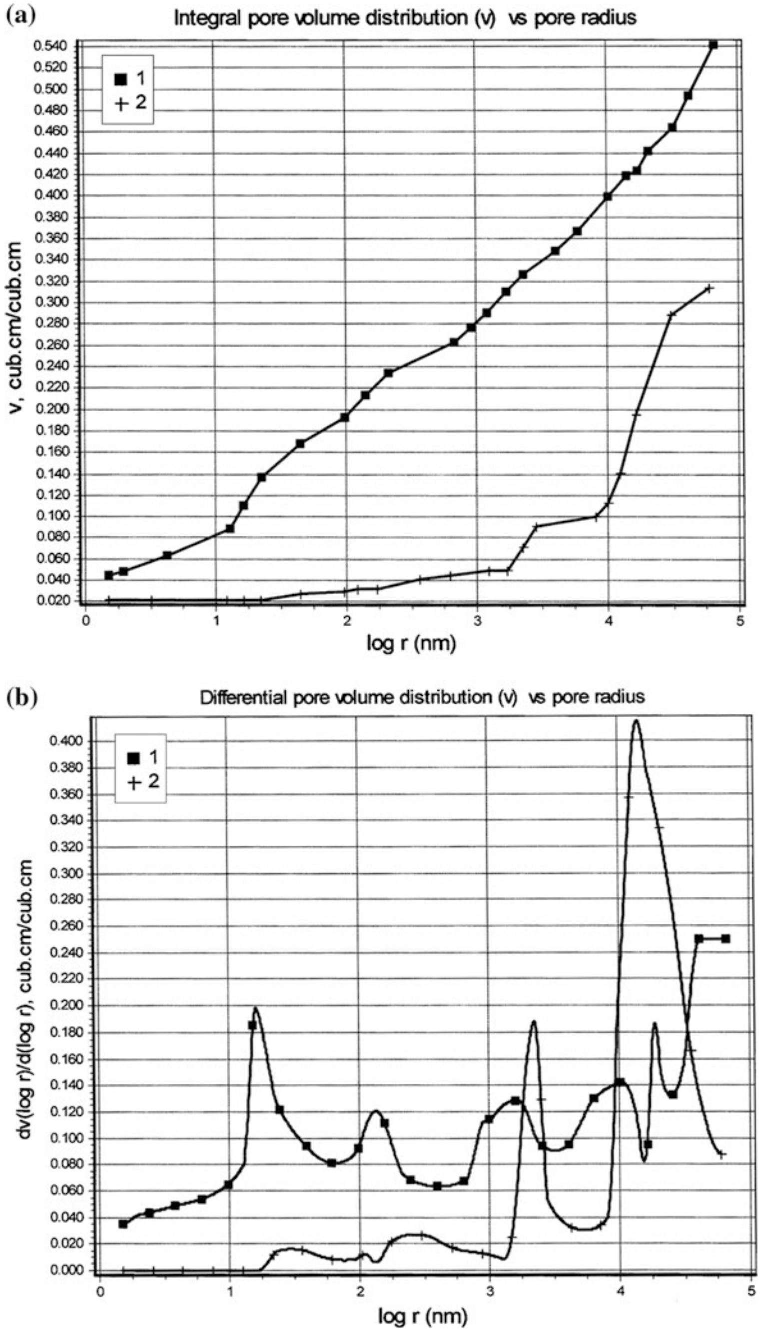


Fig. 2.2 Integral (**a**) and differential (**b**) porogramms of banknote paper measured in water *1* and octane *2*

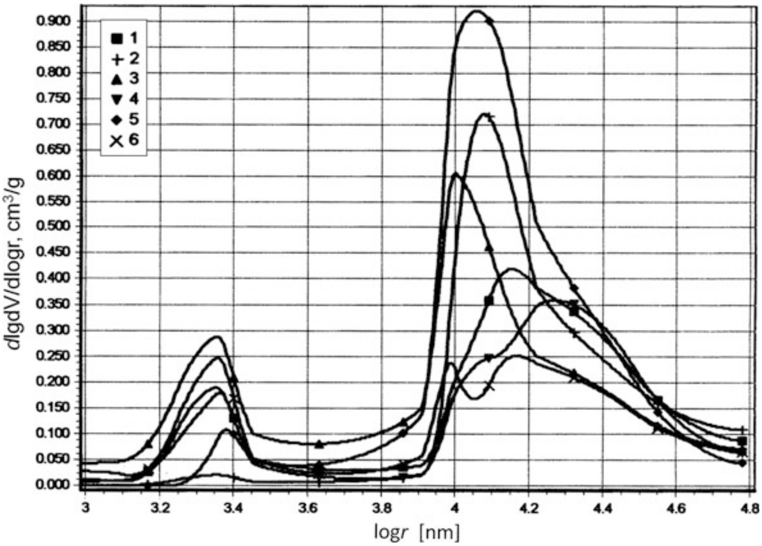


Fig. 2.3 Differential porometric curves for 6 samples of banknote paper measured in octane

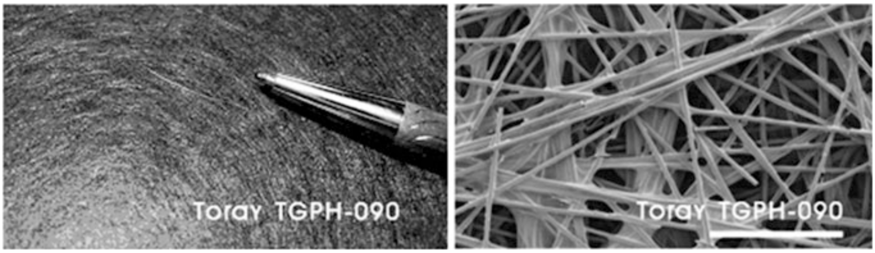


Fig. 2.4 Electron microscopy images of carbon paper of Toray type—TGPH—090

As we can see, in a dry state characterized by octane curve, the porosity of a banknote is 31 % and the pore radius range extends from about 20 nm to 65 μm; the main peaks in the differential curve occur in the pores with $r \sim 2.5$ and 20 μm. When immersed in water the banknote swells strongly to porosity 54 %, the largest incremental pore volume accounts for the small pores in the range of $r < 1$ nm to $r \sim 2$ μm. The specific surface area in the wet state (46 m^2/g) is much greater than in the dry state (0.7 m^2/g). It follows that the sorption capacity of such paper to dyes in the wet state increases sharply. Figure 2.3 presents differential porogramms measured for six different batches of banknote paper produced by one company.

As we can see, the differences in the porous structure are very sensitive identified by SCPM. This, in particular, involves the use of SCPM in forensics.

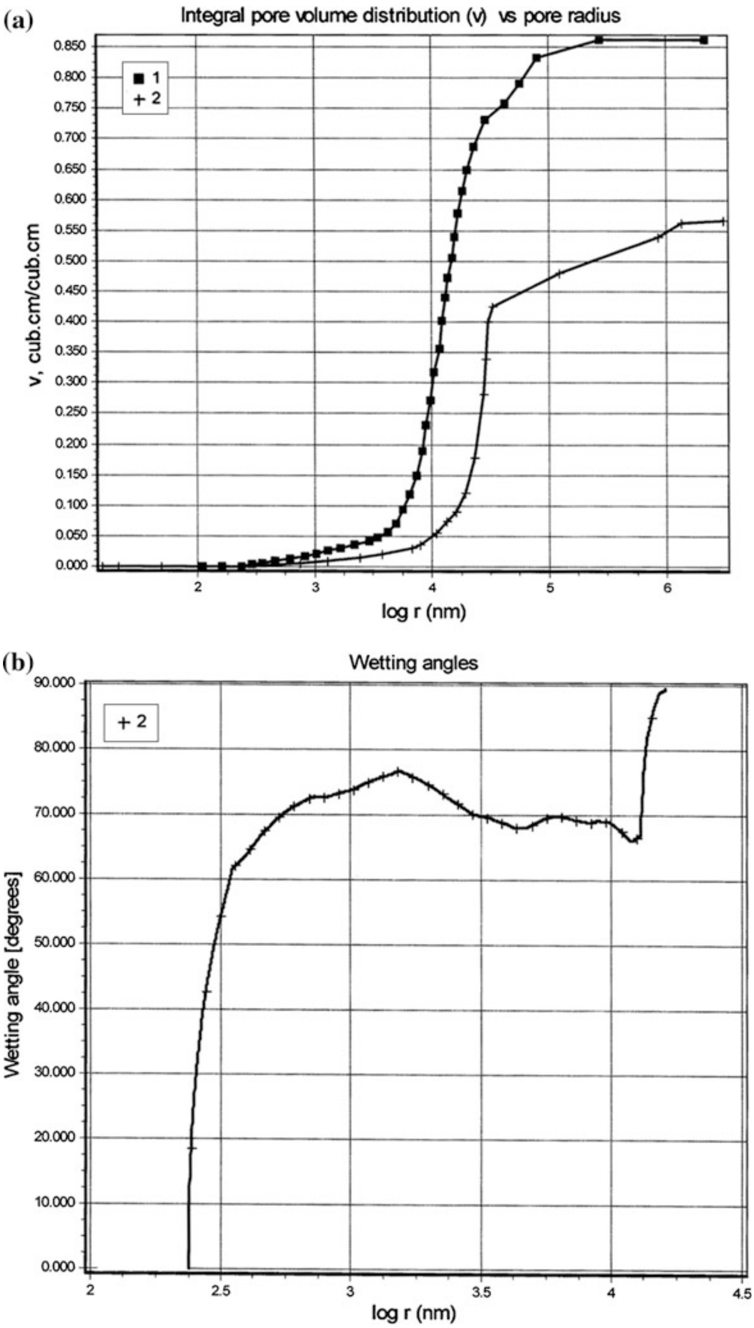


Fig. 2.5 Integral porogramms (**a**) dependence of the contact angle on pore radii (**b**) for Toray carbon paper measured in octane *1* and water *2*

2.7 Carbon Paper of Fuel Cell

One example of paper made from carbon fibers is a sheet heater. There is an ordering of carbon fibers orientation to produce different heating characteristics in the direction along the longitudinal and transverse axes of the heating paper, thereby expanding the possibility of using such paper. The aim of the invention is to provide a heating paper in which the pulp is added to the carbon fibers to obtain specific heating characteristics in the longitudinal and transverse directions, and the sheet heater comprises moreover, a polymeric coating, which serves as an electrical insulation. If desired, one may receive a variety of characteristics of the heater plate. A technical result of the invention is to improve the efficiency and reliability of the heater plate for long-term use.

2.8 Gas Diffusion Layer

The gas diffusion layer (GDL) is required for the implementation of current collection, for supplying reactants and discharging the reaction products from the fuel cell (see 2.1). Gas diffusion layers are usually made of carbon paper or carbon cloth, which are porous structures. Due to the presence of pores, reactant gases (H2, O2) freely penetrate to the catalytic layer. The pores serve also to remove the reaction products (water) from the cathode region. Since carbon is the electronic conductor, gas diffusion layer serves as both a current collector. Figure 2.4 shows electron micrographs of carbon paper Toray TGPH- 090.

We have studied porous hydrophilic structure and hydrophilic-hydrophobic properties of the Toray type paper. Figure 2.5a shows the integral porogramms, measured by octane (1) and water (2), and Fig. 2.5b shows the corresponding dependence of the wetting angle on the pore radius. This shows that (i) the total porosity is equal to 80 %, hydrophilic porosity is about 52 %, and hydrophobic porosity is 28 %; (ii) hydrophilic pores are not well wetted by water.

Consequently, the investigated paper has hydrophilic-hydrophobic pores. The gaseous components are delivered into the catalyst layer by hydrophobic pores, and water is discharged from a fuel cell by hydrophilic pores. The hydrophobic properties of Toray paper are caused by that it consists of a graphite fibers that is confirmed by spectra of X-ray fluorescence analysis. As it is known, graphite has hydrophobic properties. In many cases, if the carbon paper is not sufficiently hydrophobic, it can additionally be hydrophobized by suspension of water-repelling Teflon and carbon black (see Sect. 2.1).

References

1. http://www.bereg.net/
2. Volfkovich YM, Sosenkin VE, Bagotsky VS (2010) J Power Sources 195(17):5429

http://www.springer.com/978-1-4471-6376-3

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