Carbon paste electrodes in the new millennium

Invited Review

Ivan Švancara*, Alain Walcarius, Kurt Kalcher, Karel Vytřas

1Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, CZ-532 10 Pardubice, Czech Republic
2Laboratory of Physical Chemistry and Microbiology for the Environment, 54600 Villers-les-Nancy, France
3Institute of Chemistry – Analytical Chemistry, Karl-Franzens-University of Graz, A-3000 Graz, Austria

Abstract: In this review (with 500 refs), both electrochemistry and electroanalysis with carbon paste-based electrodes, sensors, and detectors are of interest, when attention is focused on the research activities in the years of new millennium. Concerned are all important aspects of the field, from fundamental investigations with carbon paste as the electrode material, via laboratory examination of the first electrode prototypes, basic and advanced studies of various electrode processes and other phenomena, up to practical applications to the determination of inorganic ions, complexes, and molecules. The latter is presented in a series of extensive tables, offering a nearly complete survey of methods published within the period of 2001-2008. Finally, the latest trends and outstanding achievements are also outlined and future prospects given.

Keywords: Carbon paste electrodes • Electrochemistry • Electroanalysis • New millennium (2001-2008)

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1. Introduction

1.1. Electrochemistry and electroanalysis with carbon paste electrodes in the light of Nobel Prize winner Jaroslav Heyrovský and his polarography

The year of 2009 comprises an anniversary celebrating exactly fifty years that have passed since Professor Jaroslav Heyrovský (1890-1967) won the Nobel Prize for Chemistry as an award for the discovery of polarographic method, its principal development, and popularisation worldwide [1]. Coincidentally, the same year also represents a break-point that indicates the start of a new half-a-century of existence of carbon paste as the electrode material [2].

It is to be noted that both seemingly distant fields – i.e., polarography with the dropping mercury electrode (DME) and electrochemistry with carbon paste electrodes (CPEs) – are somehow associated as the configuration of classical DME has become an inspiration for similarly functioning electrode variant based on carbon dispersion. This linking point had appeared in the late 1950s, when Professor Ralph Norman Adams (1924-2002) and his students were testing a new “dropping carbon electrode” (DCE) as an alternative to the DME for anodic oxidations of organic compounds, where the mercury drop could not be used. Although such a concept had finally failed, a thicker mixture of softer consistence, carbon paste [3], was found to be capable of replacing satisfactorily the originally intended DCE configuration [4].

There is yet another link between carbon pastes and polarography – it is the first review on CPEs, written again by Adams [5] that had appeared in a Japanese bulletin Review of Polarography. In view of present day’s classification, it was rather unusual...

* E-mail: Ivan.Svancara@upce.cz
choice as the referred CPEs representing solid-like sensors, with invariable surface, and of non-mercury character could not be operated in the polarographic regime, but voltammetrically. (At that time, however, voltammetric experiments had sometimes been reported as polarographic measurements – see e.g. [6] and the authentic citation withdrawn from the abstract, “...The carbon paste electrode recommended by Adams for polarographic oxidation of various organic substances...”, published in Nature – one of the most prestigious scientific journals.)

Finally, polarography with DME and the CPEs themselves share quite similar fates when taking into account their more-or-less accidental discoveries, as well as the resultant position achieved in modern electrochemistry. Whereas polarographic I-E curves were first registered during investigations with electrocapillary phenomena at the DME [7], carbon paste was a “side-product” coming from unsuccessful experimentation with the above-mentioned DCE [4,5]. Some decades later, when polarography had already become the worldwide-renowned scientific discipline [1], the electrochemistry with CPEs also started to play a role of highly respected field that would spread over the globe, spawning about 2 000 scientific papers and having touched almost each area of theoretical and applied electrochemistry [2].

1.2. The state of art in the new millennium

Since their invention in 1958, carbon paste electrodes (CPEs) underwent a very impressive development, pursuing the progress in electrochemistry, electroanalysis, and instrumental analysis as such. The respective history illustrated via the individual periods and milestones has already been summarised, when practically each aspect, feature, or particular area were of interest in the past five decades. Also, some significant periods of research work with CPEs were the subject of exclusively oriented reviews and related reports (see [1,2] and refs. therein).

Herein, for the reader’s comfort, it is possible to briefly point out the respective bibliographic sources published to date and given below in a chronological order: (i) the early era of CPEs has been evaluated by Adams himself [4,5]; the key contributions from the 1960s concerning initial characterisations of CPEs coming also from his laboratories [8-10], as well as from some other pioneers in the U.S. and Europe [11-15]; (ii) typical achievements during the 1970s can then be withdrawn from some original reports (e.g. [16-20]); (iii) the starting era of chemically and biologically modified carbon paste electrodes (CMCPEs and CP-biosensors, respectively) initiated by a series of key studies [21-25] and spread over the entire 1980s is documented by a triad of contemporary reviews [26-28]; (iv) the beginning of 1990s and the following years are covered in the remaining reviews articles [29-39], including some specialised areas [34,35]. Finally, there are also two attempts to overview the field in its entirety. The first accomplishment of this kind is a 250-pages-lengthy chapter published in the Encyclopedia Of Sensors (EOS) series [40]; the second being a brand new review made on the occasion of the half-centurial jubilee of carbon paste [2]. As seen, the last review devoted to a particular period of the field was the article published by our group in 2001 [36].

In an effort to specify the latest achievements and trends, we have prepared this new review focused on the years after the commencement of the new millennium – for the period of 2001-2008. In some respect, it can be considered as a continuation of the above-mentioned review covering the years of 1996-2000 [36], together with its forerunners having dealt with the preceding half-decade of 1991-1995 [29,30]. However, compared to these compilations, there is one distinct difference – this review and its sections concerning electroanalytical applications are concentrated on inorganic analysis only and the determinations of organic substances, environmental pollutants, pharmaceuticals, and biologically important compounds are not considered, except for single mentions dealing with new groups of CPEs or in association with latest achievements with some particular techniques. The reason for such a selection is a special review [41] covering the recent advances in organic and biological electroanalysis with CPEs and appearing soon in an article dedicated also to the 50th anniversary of Heyrovsky’s Nobel Prize and concerning predominantly organic electrochemistry.

Last but not least, here is only a little overlay with the above-mentioned book-chapter [40], having also reviewed a number of publications from the first years of the new millennium. This text is focused exclusively on latest trends and summarises additionally more than two hundred new publications that have appeared in the last three years – i.e., after the release of the review in EOS.

2. Electrochemical research with carbon paste electrodes in the period of 2001-2008

2.1. Classical carbon pastes and some advances in their characterisation

Similarly as in previous decades, mixtures made of commercially available spectroscopic graphite powders (as a carbon moiety) and of either paraffin (mineral) oils