

## Physicochemical techniques in the investigation of electrochemical cells\*

**O. A. Mashkin\*\***, Y. V. Kuzminskii and Y. A. Maletin

*Institute of General and Inorganic Chemistry, Kiev (U.S.S.R.)*

(Received July 10, 1990; in revised form September 29, 1990)

### Abstract

This paper reviews physicochemical (mainly spectral) methods employed to investigate processes taking place in high-energy batteries and to test active components and construction materials. Using specified techniques, various problems pertaining to selection of electrode materials and the creation of the battery as a whole, can be solved. The applicability of various techniques to problem solving is analysed.

### Introduction

High-efficiency electrochemical cells (EC), especially ECs of the new generation, are being developed in the region of overlap and between different fields of chemistry; therefore, the speedy and successful solution of problems is difficult when electrochemical techniques alone are used in the investigation. Almost from the very early stages of the development of lithium ECs, investigators have tried to employ physicochemical techniques: the range of these techniques is now extremely wide and continues to widen. They include various spectroscopic techniques that are used to solve problems connected with the development of ECs, whether it be the choice of construction materials or the determination of the nature of reaction intermediates and end products. Since none of the techniques employed can give comprehensive information, in recent years a tendency has developed to use a combination of techniques. Electrochemical procedures form the basis, but a wide range of spectral techniques (from X-ray spectroscopy to radiospectroscopy), calorimetry, chemical analysis, etc., are employed in combination with them. Such investigations can give a complete picture of the processes taking place in an electrochemical system, opening up the possibility of developing methods to control electrode processes. The aim of the present paper is to review physicochemical techniques which are useful when investigating processes that occur in ECs.

---

\*Paper presented at the 5th International Meeting on Lithium Batteries, Beijing, China, May 28–June 2, 1990.

\*\*Author to whom correspondence should be addressed.

## **X-ray diffraction**

This appears to be the most frequently used of the techniques known to date. It is used mostly in the investigation of rechargeable EC cathodes to follow structure changes in the positive electrode during cycling. To this end, X-ray phase analysis [1–13] of discharged and original samples, followed by a comparison of the lattice parameters, is generally employed. Of special interest in this respect are the investigations of McKinnon and Dahn [14, 15], who developed a method of obtaining a diffraction pattern directly from the species formed in an electrochemical cell by the intercalation of lithium ions into the cathode structure; this allowed them to overcome the influence of side effects associated with the transfer of a sample from the electrochemical cell to the diffraction analysis cell.

A number of investigators have successfully used X-ray studies in combination with other physicochemical techniques. For instance, the application of NMR spectroscopy enabled the mechanisms of nickel and iron electroreduction processes in the phosphorus trisulphides of these metals to be elucidated more exactly [16], and optical microscopic analysis allowed a study of the intercalation of lithium into cathodes based on a number of transition metal chalcogenides and oxides [17]. The effectiveness of the use of X-ray diffraction may also be illustrated by the fact that some patents concerned with the selection of cathodically-active materials cite X-ray study data as one of the main criteria for choice [18–20].

By comparison, anodic materials have been little studied roentgenographically. However, ref. 21 may be cited as an example, reporting a technique for studying the properties and structure of films on lithium in an aprotic electrolyte. Investigations using this technique were carried out without extracting lithium from the solution: this ruled out the possibility of a change in film composition on transfer of a sample from the solution to the equipment for X-ray study.

## **Energy dispersive analysis by X-rays (EDAX)**

This procedure has seldom been used because of the difficulty involved in its operation. The technique was mainly employed to investigate the structure of chalcogenides used as secondary EC cathodes [22, 23]. Interesting results were obtained when the method was used in combination with secondary ionic mass spectrometry and electron spectral methods of analysis [24]. The use of a combination of these techniques allowed the authors of the above paper to determine the phase composition and structure of lithium-intercalated products at various stages of the electroreduction of  $\text{MoO}_3$  film in an aprotic electrolyte.

## **X-ray photoelectron spectroscopy (ESCA)**

Of the techniques associated with the adsorption of X radiation, this is of greatest interest. By combining this method with IR spectroscopy, the

authors of ref. 25 investigated the surface of a lithium anode in a number of aprotic organic electrolytes. To study cathodic materials, XPS was used in combination with the X-ray technique [26]. This confirmed that  $M^{5+}$  ions are reduced to  $M^{4+}$  on the electroreduction of vanadium and niobium pentoxides, and that Li–O bonds, which have a more ionic character than those in the  $Li_2O$  oxide, appear in the structure of the compound. Moreover, the ESCA technique was used by the authors of a patent [27] as the main criterion for the choice of polyaniline as the cathode of a secondary EC.

The application of the EXAFS technique (extended X-ray absorption fine structure) [28] to the study of ECs appears to be very promising. This procedure enables one to obtain information on the nearest neighbours of mobile ions in the material under investigation and can be employed to study both electrolytes and intercalated cathodes. However, its extensive application is unfortunately limited at the present time.

### The infrared technique

This is widely used to study the processes occurring in ECs. It is primarily employed to analyse current-producing reaction products and intermediates, and is especially informative in the study of organic and organometallic compounds. For instance, when studying polypyrrole-based electrodes [29] stored for an extended period, it was revealed that the number of strong lithium–polypyrrole bonds decreased and the number of weak bonds increased with time. These observations made it possible to predict the shelf life of ECs and to develop methods for reducing the self-discharge of such electrodes.

Investigations of the products of sulphur dioxide discharge in acetonitrile [30] and thionyl chloride [31] resulted in the identification of some of the reaction products (e.g., hydrocarbons such as methane and ethylene in the former case). However, it was concluded that the data of IR spectroscopy alone are insufficient to characterize the compounds that are formed during discharge.

Use of the infrared technique gives interesting results when studying the distribution of reaction products over the bulk of a cell. In combination with the vacuum extraction method, this allowed construction of a model for diffusion processes occurring in a lithium/thionyl chloride cell [32]. As in the case of X-ray phase analysis, this procedure is used in patent literature as a criterion for the selection of cathodic materials [33, 34].

The infrared technique is less often used for the investigation of cathodes based on inorganic compounds; it allowed, for example, the electroreduction processes of vanadium oxide electrodes to be studied. It was used to follow the change in Li–O and V–O bond strength at various discharge stages, and to determine that vanadium with an oxidation state of 4+ can be formed [35]. It was also concluded that the crystal structure of the oxide is disordered and changes during discharge, leading to an increase in polarization and ohmic resistance and giving rise to several plateaux in the discharge curve [36].

## Other spectroscopic methods

Raman [37] and micro-Raman spectroscopic [38] techniques have been successfully employed to identify intermediates when discharging thionyl chloride cells at low currents. The procedures are not yet practised on a large scale, however.

In contrast to the X-ray technique, vibrational spectroscopy can be used not only to investigate cathodic and anodic materials but also to study processes occurring in an electrolyte. For instance, the solvation and association of a number of alkali salts in dimethyl formamide was studied with the aid of IR spectroscopy [39]. This technique is also employed for analytical purposes, e.g., to determine the water content of EC electrolytes [40].

The use of spectrophotometry for analytical purposes may also be mentioned [41]. Optical absorption spectra were used to study the reduction of cathodic materials based on tantalum disulphide [42], and on phosphorus trisulphides of some transition metals [43] with a model agent — *n*-butyllithium.

Radiospectroscopic techniques have only recently been employed in EC investigations, but they have not yet found wide use.

### *Electron spin resonance (ESR)*

This was found to be useful [44] in the study of the electroreduction of sulphur dioxide in the presence of lithium and alkylammonium salts. It was possible to detect radical intermediates and to show that the electroreduction process occurred via the free radical formation stage. It was also shown that the tetraalkylammonium cation was involved in the current-producing reaction. Later, these investigations were supplemented by a chromatographic study of complete- and partial-electroreduction products [45]. The ESR technique was used in combination with IR spectroscopy to establish the electro-reduction sequence for metal–ligand fragments in tetraazomacrocyclic complexes [46].

### *Nuclear magnetic resonance (NMR)*

This technique was mentioned earlier. In addition, in ref. 47, an attempt was made to connect the electroreduction potentials of different polyfluorocarbon structural modifications to structural parameters, the NMR method being used in combination with X-ray and chemical analysis. This approach determined that the polyfluorocarbon cathodic reduction overpotential decreased with increasing layer spacing.

The use of secondary ion mass spectroscopy in the study of electrochemical processes was also mentioned above. One further possible use of this technique was reported in ref. 48, where information on the composition and structure of passivating films on a lithium electrode is presented. Due to the increasing number of studies concerned with lithium electrodes, and the development of methods for their protection, the role of this technique will undoubtedly increase.

## Calorimetric and microcalorimetric techniques

These have found increasing favour because of their relative simplicity. Using them, the compatibility between the structural materials and components of electrochemical systems (especially with liquid oxidants) [49, 50] and the self-discharge of a cell as a whole have been determined [51–53]. When *n*-butyllithium is used as the model agent, the calorimetric technique is also suitable for studying the reduction of solid cathodic EC materials [54, 55]. For instance, an intermediate cathode discharge stage was revealed by microcalorimetry of partially discharged copper sulphide samples [55].

Still more interesting results can be obtained when calorimetry is employed to study processes occurring in ECs with liquid oxidants. For example, the use of calorimetric data for newly filled thionyl chloride- and sulphur dioxide-based cells enables the e.m.f. and activation energy of cells to be calculated [56, 57]. Further, direct calorimetric measurements during discharge allowed data on the calorific power of the system to be obtained, and the establishment of safe service conditions for thionyl chloride cells [58].

Of the non-electrochemical techniques whose employment in the investigation of ECs is still uncommon, the radiochemical procedure for studying adsorption on electrodes is noteworthy: it has been used to investigate the lithium/thionyl chloride system [59, 60]. A method for determining the service life of batteries by measuring the dielectric constant, followed by a comparison with the standard values was patented [61]. This method can also be applied to thionyl chloride cells.

The employment of Mössbauer spectroscopy to study current-producing processes in ECs is still uncommon. It can only be used to investigate compounds containing iron, tin, nickel, tellurium, and other ions. The electroreduction of iron oxides by lithium ions [49], and the structure of the reaction products, have been studied by this technique.

A holographic interferometry technique has been employed [62] to check the cell volume variation, particularly of a lithium/iodine-based EC.

Reference 63 describes an attractive method to determine the temperature distribution in thionyl chloride-type ECs during discharge. The essence of the method consists of applying a liquid-crystalline film, which can change its colour over a wide range depending on the object temperature, to the cell surface.

Papers in which a combination of techniques has been successfully employed to study processes occurring during the discharge and storage of ECs should be specially noted. The paper presented by Avrosham at the conference on EC problems in 1984 [63] must be mentioned. His paper gave much prominence to the use of diffraction techniques in the study of the direct intercalation of lithium cations into a cathodic material under discharge conditions. The author also considered methods for the study of the corrosion of active and structural EC materials and methods for analysing EC discharge products.

Almost all the remaining noteworthy papers deal with investigations into thionyl chloride- and sulphur dioxide-based ECs. Since the objective of most investigators was to detect and identify reaction intermediates and end products, the main techniques were electronic and IR spectroscopy in combination with ESR. The use of IR spectroscopy revealed the presence of partially reduced thionyl chloride (in addition to  $\text{SOCl}_2$ ,  $\text{SO}_2$ , and  $\text{SO}_2\text{Cl}_2$ ) and such compounds as  $\text{S}_2\text{O}$ ,  $\text{Cl}_2\text{O}$ ,  $\text{S}_2\text{Cl}_2$ ,  $\text{SCl}_2$  in solution, and the sequence of their appearance in solution. The application of ESR to quickly frozen samples showed the presence of the  $\text{SOCl}^\cdot$  radical in solution, which is then reduced to  $\text{SCl}_2$  and  $\text{SO}_2$  [65]. In some cases, these investigations were supplemented by an analysis of the lithium electrode surface using scanning electron microscopy [66] and the XPS technique [67]. Gas chromatography and atomic adsorption spectroscopy were used to analyse the products formed on reversal of the polarity of the  $\text{Li}/\text{SOCl}_2$  cell [68], in addition to the techniques cited; this confirmed the involvement of the electrolyte in redox reactions and its oxidation to  $\text{SO}_2$ ,  $\text{Cl}_2$ ,  $\text{SCl}_2$ , and  $\text{S}_2\text{Cl}_2$ . With the same objective, Abraham and Ritts [67] supplemented the techniques cited with mass spectrometry and electron microprobe analysis when studying the state of the  $\text{Li}/\text{SiO}_2$  system at various degrees of discharge.

Examination of the data obtained during these investigations suggests a comprehensive system of chemical and electrochemical processes that occur during the discharge of an EC to different degrees and at different current densities.

## Conclusions

The above information illustrates the capabilities of physicochemical techniques in studying processes occurring in ECs and the prospects for their employment. It is evident that the role of physicochemical techniques will increase further. The particular technique to be applied will depend on the objective of the investigator.

## References

- 1 P. J. Mulhern and R. R. Haering, *Can. J. Phys.*, **62** (1984) 527–531.
- 2 Yamanaka Shofi, Ohashi Masao, Sumihara Masanori and Hattori Mahoto, *Chem. Lett.*, no 8, 1403–1406.
- 3 R. P. Barinskii, Y. P. Shevchenko, M. M. Kulikova, A. S. Golub, Y. N. Novikov and M. Y. Volpin, *Dokl. Akad. Nauk SSSR*, **274** (1984) 1381–1384.
- 4 J. Marek, Inan Mohyla, NII Kh., no 52, 30 p, *Tesla Electronics*, **12** (1979) 67–73.
- 5 F. Bonino, S. Morzilli and B. Scrosati, *J. Power Sources*, **14** (1985) 65–69.
- 6 H. Whittingham and Snanley, *J. Electrochem. Soc.*, **123** (1976) 315–320.
- 7 S. Venosono, S. Kikkawa and M. Koizumi, *Mater. Res. Bull.*, **20** (1965) 259–263.
- 8 N. Kumagai, K. Tanuo and N. Kumagai, *Prog. Batteries Solar Cells*, **4** (1982) 12–13.
- 9 Ohzuku Tsutomu, Kodama Takahiro and Hirai Taketsugu, *J. Power Sources*, **14** (1985) 153–166.

- 10 J. B. Goodenough, K. Mizushima and T. Takeda, *Jpn. J. Appl. Phys.*, 19 (1980) Suppl. 3; *Proc. 4th Int. Conf. Ternary and Multinary Compounds, Tokyo, Aug. 27-29, 1980*.
- 11 J. M. Tarascon, *J. Electrochem. Soc.*, 134 (1987) 1345-1351.
- 12 M. V. Ptitsyn, K. I. Tikhonov and A. L. Rotinyan, *Elektrokhimiya*, 16 (1980) 737-740.
- 13 E. Wang, N. Kimura and M. Greenblatt, *J. Electrochem. Soc.*, 132 (1985) 1505-1506.
- 14 W. R. McKinnon and J. R. Dahn, *Solid State Commun.*, 52 (1964) 245-248.
- 15 J. R. Dahn and W. R. McKinnon, *J. Phys. C; Solid State Phys.*, 17 (1984) 4231-4243.
- 16 R. Brec, M.-H. Whangbo, G. Fadseas and G. Quvrad, *3rd Int. Meet. Lithium Batteries, Kyoto, 27-30 May, 1986, Ext. Abstr., S.F.*, (1986) 309-312; *J. Power Sources*, 20 (1987) 205.
- 17 M. Whittingham, Stanley, Chianelli Russell, *Proc. 8th Int. Symp. Reactive Solids, Goteborg, 1976, New York-London, 1977*, 89-94, Discuss., p. 94.
- 18 *U.S. Patent 4 247 608* (Jan. 27, 1981).
- 19 *Aut. svidetelstvo no 867 333* (1981).
- 20 *U.S. Patent 4 702 977* (Oct. 27, 1987).
- 21 Nazri Gholamabbas and R. H. Muller, *J. Electrochem. Soc.*, 132 (1985) 1385-1387.
- 22 Guo Chang-Lin, Lu Chang-Wei, Shen Ding-Kun and Yu Zhizhong, *Acta Phys. Sin. Abstr.*, 34 (1985) 1336-1341.
- 23 Onuki Yishichika and Inada Rumuko, *Tech. Rep. ISSP, 1981, A*, no 1127, 25 pp.
- 24 N. S. Vereshchagina, K. A. Tikhonov, I. S. Kotousova and G. M. Guryanov, *Elektrokhimiya*, 18 (1982) 1134-1137.
- 25 S. P. S. Yen, D. H. Sheen, R. R. Vasepnez and B. F. Catter, *Proc. Symp. Lithium Batteries, Washington, DC, Oct. 9-14, 1983; Bennington, IBPPT and KhEVZ*, 32 (1988) 15-20.
- 26 N. Kumagai, K. Tanno, T. Nakajima and N. Watanabe, *Electrochim. Acta*, 28 (1983) 17-22.
- 27 Fuzita Kazunori, Sutimoto Haroyuki and Toyama Audio, *Japan Patent Applic. 62-29 065* (Feb. 7, 1987).
- 28 R. G. Linford, Solid state batteries, *Proc. NATO Adv. Study Inst., Alcabideche, Portugal, Sept. 2-14, 1984*, pp. 509-512. Discuss., 513.
- 29 S. Panero, D. Prospero, F. Bonino, B. Scrosati and A. Corradini, *Electrochim. Acta*, 32 (1987) 1007-1011.
- 30 H. V. Venkatesetty, W. Ebner, D. L. Chua and W. P. Kilroy, *Proc. Symp. Lithium Batteries, Washington, DC, Oct. 9-14, 1983, Electrochem. Soc., Pennington, NJ, 1985*, pp. 276-292.
- 31 O. R. Schleikeyer, P. G. Garvy and A. Lombardi, *Prog. Batteries Solar Cells*, 5 (1984) 302-306.
- 32 D. Vallin and Ph. Chenebanu, *J. Power Sources*, 17 (1986) 353-360.
- 33 Fudzii Tanafumi, Morita Akikatsu et al., *Japan Patent Applic. 62-145 653* (June 29, 1987).
- 34 Lecerf Ardre, Gipelec, *Fr. Patent Applic. 2 557 734* (July 5, 1985).
- 35 K. Wiesener, W. Schneider, D. Ilic, K. Steger and K. H. Hallmeier, *J. Power Sources*, 20 (1987) 157-164.
- 36 K. Wiesener, W. Schneider, D. Ilic and E. Brackmann, *3rd Int. Meet. Lithium Batteries, Kyoto, Japan May 27-30, 1986, Extended Abstr., S.I., 1986*, pp. 195-200.
- 37 M. C. Dhamelincourt, F. Wallart, P. Barbier and G. Mairesse, *J. Power Sources*, 14 (1985) 77-82.
- 38 M. C. Dhamelincourt and F. Wallart, *J. Power Sources*, 20 (1987) 69-73.
- 39 V. S. Osipov and I. S. Perelygin, Probl. solvatatsii i kompleksobraz. v rastvorakh, *Tezlay Dokl. 3 Vses. Soveshch., Ivanovo, June 27-29, 1984, Vol. 1, Ivanovo, 1984*, p. 136.
- 40 R. Jasinsky and C. Carrol, *Anal. Chem.*, 40 (1968) 1903-1909.
- 41 J. Raymond, C. Susan, ? Laboratories, Inc., Waltham, MA, 02154.
- 42 A. M. Ghorayeb, W. Y. Liang and A. D. Yoffe, *J. Phys. C: Solid State Phys.*, 19 (1981) 7323-7328.
- 43 R. Brec, D. Schleich, A. Louisy and J. Rouxel, *Ann. Chim. (Fr.)*, 3 (1978) 347-352.
- 44 A. Anantaraman, P. Archambault, R. Day and C. Gardner, *Proc. Symp. Lithium Batteries, Washington, DC, Oct. 9-14, 1983, The Chemical Society, Pennington, NJ, 1984*, pp. 231-243.

- 45 J. R. P. Godin, M. Farrington and C. L. Gardner, *Proc. Symp. Lithium Batteries, Washington, DC, Oct. 9-14, 1983*, The Chemical Society, Pennington, NJ, 1984, pp. 255-264.
- 46 A. V. Gorodyskii, E. V. Kuzminskii and O. A. Mashkin, *11th Conf. Coordination Chemistry, Bratislava, June 2-5, 1987*, pp. 83-86.
- 47 N. Watanabe, R. Hagiwara and T. Nakajima, *J. Electrochem. Soc.*, 191 (1984) 1980-1984.
- 48 V. M. Ovsyannikov, A. G. Demakhin and A. G. Zhukov, *V. M. Zhivotkin, Sarat. Univ., Saratov, 1988*, 12 pp.
- 49 V. N. Ponkratov, V. A. Mozalevskaya and L. A. Solomatina, *Elektrokhimiya*, 25 (1989) 299-300.
- 50 F. B. Tudron, *J. Electrochem. Soc.*, 128 (1981) 516-520.
- 51 Zh. Sonj, Ch. Xic, Q. Xu and S. Qu, *Jwukan Univ. (Natur. Sci. Edn.)*, 77 (1988) 78-81.
- 52 G. M. Bergman, S. J. Ebce, E. S. Takeuchi and P. Keister, *3rd Int. Meet. Lithium Batteries, Kyoto, May 27-30, 1986, Ext. Abstr., S.I., 1986*, pp. 125-128.
- 53 G. M. Bergman, S. J. Ebel, E. S. Takeuchi and P. Keister, *J. Power Sources*, 20 (1987) 179-185.
- 54 F. Dalard, D. Deroo and H. Djellab, *J. Power Sources*, 14 (1985) 71-75.
- 55 L. Chow, *J. Electrochem. Soc.*, 134 (1987) 403.
- 56 Kim Kwang, Y. C. and L. Chua David, *Prog. Batteries Solar Sens.*, 4 (1982) 58-61.
- 57 R. Y. Kim, *Prog. Batteries Solar Cells*, 6 (1987) 89-92.
- 58 N. A. Godshall and J. R. Driscoll, *Proc. Symp. Lithium Batteries, Washington, DC, Oct. 9-14, 1983*, The Chemical Society, Pennington, NJ, 1984, pp. 171-183.
- 59 V. P. Bosov, Y. A. Karapetyan, A. D. Krysenko, A. N. Chuvasakin and Y. A. Rogachov, *Elektrokhimiya*, 21 (1985) 558-560.
- 60 *U.S. Patent 4438182*, (May 20, 1984).
- 61 L. C. Phillips, R. G. Kelly, J. W. Wagner and P. J. Moran, *J. Electrochem. Soc.*, 133 (1986) 1-5.
- 62 J. R. Driscoll and S. Szpak, *J. Power Sources*, 14 (1985) 321-328.
- 63 K. M. Avrasham, *Solid State Batteries, Proc. NATO Adv. Study Inst., Alcabideche, Portugal, Sept. 2-14, 1984*, Dordrecht, 1985, 293-296.
- 64 R. Williams, F. Tsay, S. Kim, M. Evans, Q. Kim, A. Rodriguez, B. J. Carter and H. Frank, *Proc. Symp. Lithium Batteries, Washington, DC, Oct. 9-14, 1983*, The Chemical Society, Pennington, NJ, 1985, pp. 60-79.
- 65 S. Subbarao, D. Lawson, H. Frank, G. Halpert, J. Barnes and R. Bis, *J. Power Sources*, 21 (1987) 227-237.
- 66 N. A. Fleischer, S. M. Manske and R. J. Ekern, *Proc. Symp. Lithium Batteries, Washington, DC, Oct. 9-14, 1983*, The Chemical Society, Pennington, NJ, 1985, pp. 90-102.
- 67 B. J. Catter, R. M. Williams, M. Evans, Q. Kim, S. Kim, Tsay F. and H. Frank, I. Stein, *Proc. Symp. Lithium Batteries, Washington, DC, Oct. 9-14, 1983*, The Chemical Society, Pennington, NJ, 1984, pp. 162-170.
- 68 K. M. Abraham and L. Ritts, *Proc. Symp. Lithium Batteries, Washington, DC, Oct. 9-14, 1983*, The Chemical Society, Pennington, NJ, 1985, pp. 265-275.