ELECTROCHEMICAL INCORPORATION OF LITHIUM AND SODIUM INTO CARBON BLACK

Jiri VONDRAK
Institute of Inorganic Chemistry,
Academy of Sciences of the Czech Republic, 160 00 Prague 6, The Czech Republic

Received March 22, 1995
Accepted May 15, 1995

Electrochemical insertion of sodium or lithium into carbon black electrodes from perchlorate–propylene carbonate solution occurs under formation of substances close to $C_{12}Na$ and C_6Li in potential range from 1.0 to 0 V vs alkali metal electrodes.

Graphite intercalation compounds (GIC) are the oldest known intercalation materials. The phenomenon itself was discovered just as the result of their investigation. Many reviews and books are available now on this subject[1–3]. Recently, the concept of batteries known as “rocking chair batteries” has been introduced; it comprises a rechargeable negative electrode using intercalation and deintercalation of lithium into carbonaceous material[4], mostly graphite or petroleum coke. First results show that some reaction occurs in a lithium electrolyte even with other forms of carbon[5–7]. Also the intercalation of sodium in electrochemical way into graphite occurs[8–10]. Therefore, we decided to investigate the intercalation of both metals in amorphous carbon more extensively. According to our experience, differences in behaviour of intercalation electrode material in the lithium and sodium containing electrolytes will answer this question[7,8], because the diffusion inside carbon grains would depend on the size of alkali metal cation in a different way then other reactions. Similar principle was used already for investigation of the reaction between lithium and CuO (ref.[8]).

EXPERIMENTAL

Materials and Accessories

Carbon black (Deutsche Gasrusswerke GmBH) CORAX 5 HS (100 to 110 m^2/g) were used in the mixture with 5 wt.% of polytetrafluoroethylene suspension (DuPont). According to X-ray diffraction analysis, the material was almost amorphous with extremely broad reflection line (002) at $d = 0.367$ nm only; the half-width $\beta = 3.1°$ corresponded to particle size $h = 3$ nm (using the Scherrer formula $h\ \beta \cos(\beta/2) = K\ \lambda$, where $K = 1$ is supposed[11]). The mixture was spread on a nickel screen and pressed. Typically, 0.015 to 0.03 g of mixture was applied on one electrode. 1 M $LiClO_4$ or $NaClO_4$ solutions in propylene carbonate were dried in standard way. Potentials refer to lithium or sodium reference electrodes in the same electrolyte and experiments were performed at room temperature. Cathodic constant-current chronopotentiometry was used and the results were treated by simple numeric differentiation procedure showing inflexion points of lowest slope (denoted as half-wave potentials, *E*) and those of highest slope (transition times, τ). This treatment was necessary due to insufficient separation of observed processes on the curves. Potentials refer to lithium or sodium, respectively.

Several electrodes were immersed to the electrolyte and short-circuited to alkali metal electrode. After 3 days, they were rinsed rapidly with cyclohexane and leached in water; the amount of generated alkali was found volumetrically by the solution of H_2SO_4 (0.1 mol/dm^3). Rapid evolution of gas occurred during the treatment in water.

RESULTS AND DISCUSSION

The electrodes, if short-circuited to alkali metal, accepted alkali metal at rather high rate (initial current approximately 10 mA/cm^2). The final composition corresponded to $x = 0.084$ (expressed as CNa_x) or $C_{11.9}Na$ in the case of sodium; corresponding numbers were $x = 0.175$ or $C_{5.7}Li$ in the other case. These values are close to those in graphite (stage 1 for the lithium intercalation compound and stage 2 for sodium one).

Typical chronopotentiograms obtained in lithium and sodium electrolytes are shown in Fig. 1 (the example of sodium is an inclusion).

A main process appears on the cathodic chronopotentiometric curves and it is preceded by another one, which was not well developed and which caused the necessity of the numerical treatment mentioned above. Their properties are summarized in Table I. The first process occurs at 1.65 to 1 V (against Li) and it is shifted slightly more negative in sodium systems. The specific charge of the first wave was 220 μC/cm^2 in lithium and 360 μC/cm^2 in sodium electrolytes, which corresponds to just one or few

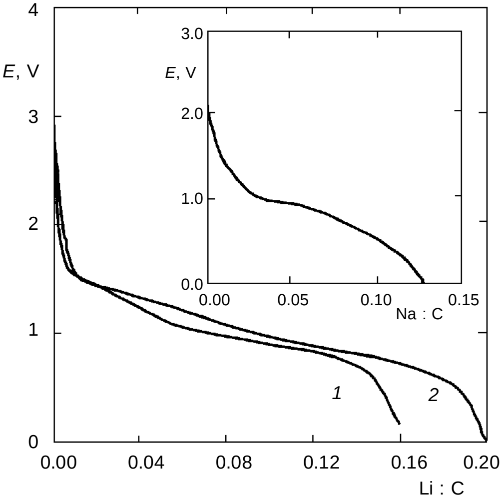

FIG. 1

Chronopotentiograms of carbon black in 1 M $LiClO_4$ electrolyte. Parameter *x*: charge (in F/mol of C). Current load: *1* 3.0 mA/g, *2* 8.2 mA/g. Insert: Chronopotentiograms of carbon black in 1 M $NaClO_4$ electrolyte, current load 5.9 mA/g monolayers. However, the numeric procedure cannot ensure proper deconvolution of both processes. The charge of the second wave is evaluated from its length and it is expressed as apparent stoichiometric coefficient x (in the compound CM_x in Table I under assumption that all current is used for alkali metal insertion into graphite; it does not change much at low current load. The limiting value is not much different from the results obtained by chemical analysis.

The specific surface area of used carbon black is 100 to 110 m^2/g. If spherical particles and density $d = 2$ g/cm^2 are supposed, then an effective particle radius $\rho = 14$ nm should be estimated. As we see from Table I, the charge of wave 1 does not vary too much for current loads below 0.1 A/g, i.e., for time duration τ of that wave exceeding 10 to 50 s. For a diffusion in a spherical body, the whole bulk is accessed by diffusion

TABLE I
Chronopotentiometry of carbon black in $LiClO_4$ and $NaClO_4$ electrolytes

m, g	i, A/g	$E1$, V	$E2$, V	$q1$, $\mu C/cm^2$	x
		Lithium perchlorate			
0.0166	0.003	1.687	1.036	146	0.157
0.0122	0.0082	1.549	0.976	190	0.126
0.0225	0.0133	1.442	0.945	139	0.175
0.0185	0.027	1.383	–	351	0.048
0.0134	0.127	1.2001	–	161	–
0.0281	0.356	1.271	0.867	358	0.046
0.0202	0.495	1.245	–	95	0.0162
		Sodium perchlorate			
0.0168	0.00595	1.391	0.798	424	0.111
0.0134	0.0157	1.400	0.30	285	0.0909
0.0228	0.0219	1.2	–	599	–
0.0187	0.0428	1.1	–	49	–
0.0174	0.0575	0.82	0.45	219	0.053
0.0172	0.1163	1.089	0.448	329	–
0.019	0.526	1.045	0	146	0.0149
0.0159	0.786	1.045	<0	89	0.0136

Symbols: m mass of the electrode, i current load, E half-wave potential (against Li or Na, respectively), $q1$ specific charge (in $\mu C/cm^2$) of wave 1, x apparent stoichiometric coefficient in formula CM_x. Missing data for wave 2 indicate that the half-wave potential E was not reached for $E > 0$. Index 1 means the first wave, index 2 the wave 2 and the total amount of diffusant is constant if the condition $D\,\tau > \rho^2$ is fulfilled, and the upper limit of diffusion coefficient (D) would be $D > 10^{-18}$ m^2/s for both sodium and lithium in carbon black.

The ratio metal to carbon 1 : 12 in the case of sodium seems close to the formation of intercalation compound having stage 2, while stage 1 compound would the product of lithium insertion. This is rather in agreement of general knowledge of graphite with alkali metal intercalation compounds.

According to X-ray diffraction studies and specific surface area considerations, the carbon black contains domains with graphite structure, the average dimension of which is rather smaller than the average particle diameter. Hence, the true intercalation into these domains and rather fast diffusion along the domain boundaries should be the most probable explanation.

This paper was supported by the Grant Agency of the Czech Republic (Grant No. 203/93/0820).

REFERENCES

1. Bartlett N., McQuillan B. W. in: *Intercalation Chemistry* (M. S. Whittingham and A. J. Jacobson, Eds), pp. 19–51. Academic Press, New York 1982.
2. Ebert L. B.: Annu. Rev. Mater. Sci. *6*, 181 (1976).
3. Selig H., Ebert L. B.: Adv. Inorg. Chem. Radiochem. *23*, 281 (1980).
4. Pistoia G. (Ed.): *Lithium Batteries*, Chaps 1,2, Industrial Chemistry Library, Vol. 5. Elsevier, Amsterdam 1994.
5. Watanabe A., Mori K., Ishikawa H. and Nakamura Y.: *3rd International Meeting on Lithium Batteries*, Kyoto 1986. Abstract No. ST-14.
6. Sato K. , Noguchi M., Demachi A., Oki N., Endo M.: Science *264*, 556 (1994).
7. Vondrak J., Bludska J., Jakubec I.: J. Power Sources *14*, 141 (1985).
8. Vondrak J., Bludska J., Jakubec I.: Electrochim. Acta *37*, 603 (1992); Vondrak J., Bludska J., Jakubec I.: Presented at the *11th Conference on Power Sources, Brno 1989.* Abstract No. 6, p. 25.
9. Dey A. N., Sullivan B. P.: J. Electrochem. Soc. *117*, 222 (1970).
10. Novak P. : Electrochim. Acta *30*, 1687 (1985).