Material balance of petroleum coke/LiNiO$_2$ lithium-ion cells

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Abstract

A method is described for the estimation of the volumetric specific capacity of balanced Li-ion cells. The effect of the material balance or the cathode/anode mass ratio, r, in Li-ion cells on the volumetric specific capacity, q_v, of the electrode pair is studied in the example of a petroleum coke/LiNiO$_2$ couple. The values of q_v of several electrode pairs used in Li-ion cells, calculated on the basis of present experimental and previously published data are juxtaposed. A good agreement between calculated and experimentally determined q_v values is found. The q_v value of the natural graphite/LiNiO$_2$ pair exceeds by nearly 28% that of the commercialized PFA-C/LiCoO$_2$ pair, considered so far as the best available. This advantage will however be reduced by 30 to 50% in a real cell, when the volumes of all cell components are taken into account. The influence of r on the cycling stability is also demonstrated experimentally. The possibility of using unbalanced cells with moderately overcharged anodes appears feasible, while cells with precharged anodes from an auxiliary Li source seem impractical.

Keywords: Lithium-ion cells; Petroleum coke; Graphite; Carbon; Material balance

1. Introduction

The most spectacular achievement in the field of lithium cells in the last decade is the Li-ion battery commercialized recently by Sony Energetic Inc. [1–5]. It concluded successfully a long period of effort of many scientists aimed at developing a safe, high-energy, high-power, and long-cycling cell with a voltage sufficiently high to replace three Ni/Cd cells. The capability of a large number of carbon materials to reversibly intercalate Li and the excellent performance of three 4 V intercalation cathode materials open the prospects for the development of the Li metal-free rechargeable cell. Presently, three electrode pairs have been studied more closely: PFA-C/LiCoO$_2$ by Sony [1–5], petroleum coke/LiNiO$_2$ by Moly Energy Ltd. [6–8] and petroleum coke/LiMn$_2$O$_4$ by Bellcore [9,10]. The significance of the material balance of the petroleum coke/LiMn$_2$O$_4$ cell was pointed out first by Tarascon and Guyomard [9]. It is shown that the ratio between the masses of the cathode and the anode, r, has a considerable impact on the cell performance. It was established empirically that there is an optimum r value for this cell which can secure maximum cell capacity without any danger of Li deposition on the anode during charging.

In the present paper equations are derived for the calculation of the specific volumetric capacity q_v of any electrode pair, based on the separated charge/discharge characteristics of the anode and cathode, making the correct choice for cells with the highest volume energy density possible.

2. Experimental

High-purity petroleum coke was used as the anode material with a 0.08% ash content, 0.52% volatiles at 850 °C and 3.0 m^2/g specific (BET) surface area. The interlayer spacing $d(002) = 3.35$ Å increased to 3.41 Å after 6 h heat treatment at 1100 °C in argon. The scanning electron microscopy (SEM) picture in Fig. 1 reveals a small grain lamellar morphology. The coke powder with grain size smaller than 35 μm was teflonized by a wet process and after drying it was rolled to foils 100 ± 10 μm thick. The foils were punched to discs, 15 mm in diameter, which were pressed on copper foil discs. The anodes were dried in vacuum for 16 h at 150 °C before the cell assembly. A typical anode contained 5% Teflon, weighed 20 ± 3 mg without the current collector and had an apparent density of 1.50 ± 0.05 g/cm^3. Anodes with natural Brazilian graphite were also used in single experiments for comparison.

The cathode material Li$_x$Ni$_{2-x}$O$_2$ was synthesized at 700–750 °C from LiNO$_3$ and Ni(OH)$_2$ in an oxygen atmosphere. By variation of the Li/Ni ratio in the starting mixture, time and temperature of the thermal treatment it was possible to

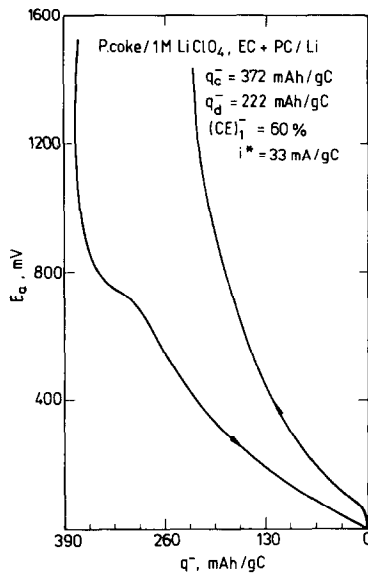Fig. 1. SEM pictures of high-purity petroleum coke.

Fig. 2. Potential profiles of a petroleum coke/LiClO$_4$, PC + EC/Li cell in the first cycle at 0.34 mA/cm^2 (33 mA/g).

obtain samples with different stoichiometries $(0.91 \leqslant x \leqslant 0.99)$ which were characterized by X-ray diffractometry (XRD) and electrochemical measurement. Details of this investigation are reported in Ref. [11]. The cathodes were prepared by pressing a blend of LiNiO$_2$ powder with 20 w/o teflonized acetylene black on an aluminium foil disc, 15 mm in diameter. A typical cathode weighed 50 ± 10 mg with an apparent density of 2.4 ± 0.1 g/cm^3.

Two electrolyte solutions were mainly used in the cells: 1 M LiClO$_4$ in a 1:1 mixture of ethylene carbonate (EC) and propylene carbonate (PC), and 1 M LiPF$_6$ in a mixture of EC and dimethyl carbonate (DMC). Two sheets of Whatman

glass fibre paper served as separators. The cycling was performed in stainless-steel laboratory coin cells provided with an Li reference electrode. The cells were cycled at constant current on computerized cyclers. Li counter electrodes were employed in the tests for the separate characterization of the anode and cathode performance. The cell assembly and the preparation of the electrolytes were performed in a dry box (< 10 ppm H$_2$O).

3. Results

3.1. Petroleum coke anode

Fig. 2 presents typical profiles of the first cycle of the anode in a petroleum coke/LiClO$_4$, EC + PC/Li cell during charge (lithiation) and discharge (delithiation) at 0.34 mA/cm^2 (33 mA/g) between 1500 and 0 mV. After a steep decay to ~ 800 mV, corresponding to a charge of 33 mAh/g, a voltage plateau at 770 mV is reached, corresponding to a charge of ~ 26 mAh/g. The potential then falls more slowly to 0 mV. The specific capacity of the first charge, estimated as average from five experiments, is $q_c = 372$ mAh/g and that of discharge $q_d = 222$ mAh/g. The coulombic efficiency in the first cycle, $CE = 60\%$ is raised to above 99% after the sixth cycle. Somewhat better results were obtained in a similar cell but with the 1 M LiPF$_6$, EC + DMC electrolyte, recently patented [12]: $q_c = 365$ mAh/g, $q_d = 233$ mAh/g, $CE = 64\%$ in the first cycle. The effect of cycling on the discharge capacity of this cell is shown in Fig. 3, curve (a). The cycling stability of the anode, CS, estimated by the expression proposed by Yamaki and Tobishima [13] for intercalation compounds:

$$q_n = q_5(CS)^{n-5} \tag{1}$$

amounts to 99.8%.

The average capacity of petroleum coke anodes in the first cycle for a mixture of two electrolytes are listed in Table 1,
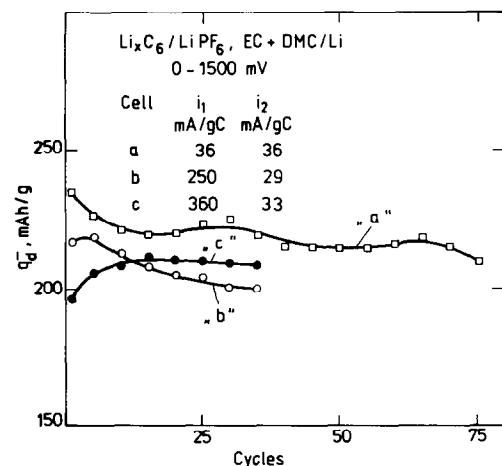

Fig. 3. Cycling test of petroleum coke/LiPF$_6$, EC + DMC/Li cells: (a) normal charging at 36 mA/g in the first cycle; (b) accelerated initial charging at 250 mA/g, and (c) accelerated initial charging at 360 mA/g.

Table 1
Capacity of different carbon anodes in the first cycle

Type of carbon	Electrolyte	q_c^- (mAh/g)	q_d^- (mAh/g)	$(CE)_1^-$ %	Refs.
Petroleum coke	1 M LiPF$_6$, EC + DEC	266	171	64	[14]
Coke 1200	1 M LiPF$_6$, EC	310	250	81	[15]
Coke 1400	1 M LiPF$_6$, EC	340	200	59	[15]
Petroleum coke	1 M LiClO$_4$, PC + DEE	250	183	77	[10]
Petroleum coke	1 M LiClO$_4$, PC + EC	372	222	60	This paper
Petroleum coke	1 M LiPF$_6$, EC + DMC	364	233	64	This paper
Natural graphite	1 M LiPF$_6$, EC + DMC	450	347	77	This paper
Natural graphite	1 M LiPF$_6$, EC + DMC	400	337	84	[16]
PFA-C	1 M LiPF$_6$, EC + DEC	450	324	72	[2,3]

together with literature data for comparison with other cokes and natural graphite.

Several authors investigated in detail the side reactions which proceed in the first charging of carbon anodes and which are responsible for the capacity loss [7,17–19]. It seems that this loss is related to two overall parasitic reactions: solvent reduction and passive film formation with some of the products of the solvent reduction. To reduce the capacity loss in the first charging is still the aim of many research groups. The most successful means is the use of organic solvents which are more resistant to reduction and cointercalation or, by the addition of crown ethers [19] which inhibit the solvent-reduction reaction.

Another possibility to lower the capacity loss is by charging the anode with a very high current in the first cycle. This approach was applied by Miura et al. [20] who charged graphite anodes by shorting them to the Li counter electrode. Indeed our experiments with petroleum coke anodes using this method resulted in a very high coulombic efficiency, close to 100%, but the self-discharge of these anodes was unacceptably high: ~60% within 100 h. It might be supposed that the passive film formed at these very high currents (initially over 60 mA/cm^2) and still 15 mA/cm^2 after 15 min is quite defective and cannot efficiently protect the anode from reacting with the organic solvents.

Experiments were carried out for an accelerated first charging of petroleum coke anodes in a 1 M LiPF$_6$, EC + DMC electrolyte but at lower initial currents, 3–4 mA/cm^2, or 250–360 mA/g. When the anode potential approached 0 mV the current was lowered and the charging continued at the normal rate of 0.34 mA/cm^2 or 33 mA/g. The CE increased moderately from 64 to 77%, but as shown in Fig. 3, (curves (b) and (c)) the cycling stability of these anodes is lower than that of a normally charged anode (curve (a) in Fig. 3).

In another experiment, a petroleum coke anode was charged in the same electrolyte to which ~300 ppm of water were added. The voltage plateau at 800 mV in this case lasted 110 mAh/g instead of 26 mAh/g as in the dry electrolyte with less than 20 ppm of water (Fig. 2). This result could be ascribed to the increased solubility of the products of the solvent-reduction reaction forming the passive film. Thus,
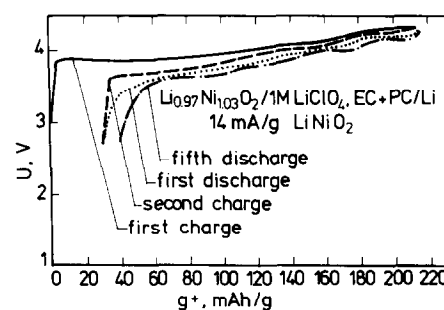

Fig. 4. Charge/discharge voltage profiles of an LiNiO$_2$/LiClO$_4$, EC + PC/ Li cell at 0.48 mA/cm^2 in the first, second and fifth cycles.

the passive film formation is retarded and the solvent reduction proceeds longer.

3.2. LiNiO$_2$ cathode

Details of the XRD data and the electrochemical performance of a series of Li$_x$N$_{2-x}$O$_2$ samples with $0.91 < x < 0.99$ were reported recently in Ref. [11]. A set of typical charge/discharge voltage profiles of a cathode with Li$_{0.98}$NiO$_2$ in the first, second and fifth cycles in a cell with an Li counter electrode and a 1 M LiPF$_6$, EC + DMC electrolyte, cycled between 4.27 and 2.6 V at 0.51 mA/cm^2, is shown in Fig. 4. Four well-expressed plateaus at 3.50, 3.60, 4.00 and 4.20 V can be discerned in the first discharge curve, marking the reversible phase transitions in Li$_x$Ni$_{2-x}$O$_2$, which coincide well with those determined by Ohzuku et al. [21] at much lower rate of discharge. As established by the same authors [21] an irreversible phase transition occurs at $x < 0.18$, resulting in a reduced cycling stability. The dependence of the charge and discharge capacities in the first cycle on the charge voltage of cathodes with $x = 0.98$ cycled at 27 mA/g down to 2.6 V is presented in Fig. 5. At the end voltage of 4.45 V the charging capacity reaches 245–250 mAh/g. Taking into consideration that the maximum charge capacity of this cathode material with $x = 0.98$ is $0.98 \times 274 = 268.5$ mAh/g, the composition at the end of the charge to 4.45 V is Li$_{0.11}$NiO$_2$. To avoid the irreversible phase formation in Li$_x$NiO$_2$ a safe upper charge limit to $x = 0.18$ should be adopted, which cor-
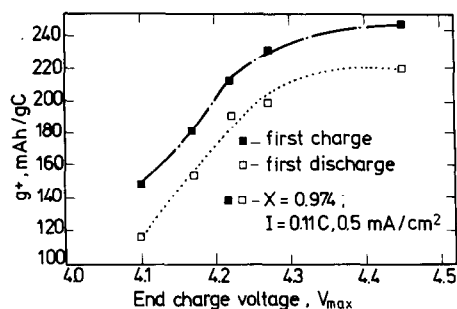
Fig. 5. Effect of the end-charge voltage on the capacity of an LiNiO$_2$ cathode cycled at 0.5 mA/cm^2 in an LiPF$_6$, EC + DMC electrolyte to 2.60 V discharge voltage.
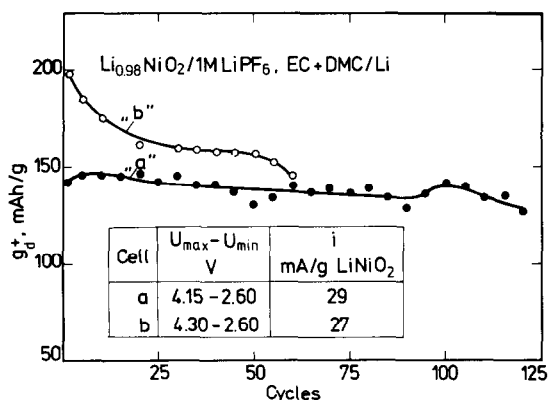

Fig. 6. Cycling tests of Li$_{0.98}$NiO$_2$/1 M LiPF$_6$, EC + DMC/Li cells with two different end-charge voltages: (a) 4.15 V, and (b) 4.30 V.

responds to 220 mAh/g in the first charge or to a maximum voltage of ~4.2 V.

Curve (a) in Fig. 6 presents the capacity decay during cycling of a cathode between 4.15 and 2.60 V at 29 mA/g, which leads to a cycling stability of $CS = 99.9\%$, estimated by Eq. (1). Curve (b) presents the decay of the discharge capacity of a cathode with the same material but cycled between 4.30 and 2.60 V at 27 mA/g. The initial capacity is considerably larger but falls much faster at a rate of 99.4%.

3.3. Petroleum coke/LiNiO$_2$ cell

In order to obtain the maximum utilization of the electrode materials in an Li-ion cell the carbon anode should be charged as fully as possible, i.e. to a potential close to 0 mV versus Li. On account of the considerably smaller specific capacity of the LiNiO$_2$ cathode in comparison with the coke anode this is achieved by an excess of the cathode mass. This excess is expressed by the ratio $r = m^+/m^-$ [10] where m^+ and m^- are the masses of the active materials in the anode and cathode, respectively.

It has been realized earlier in our experiments that the value of r is of great significance for the specific capacity and the cycling performance of the cell. In order to have a better understanding of this significance, it is necessary to consider three possible cases: (i) the balanced cell, in which the charge capacities of the two electrodes in the first cycle are equal,

i.e. $Q_c^-/Q_c^+ = 1$ or $r = r_b$, see Eqs. (2)–(4); (ii) the cell with an overcharged anode, i.e. $r > r_b$, and (iii) the case when $r < r_b$, which is possible if the anode is partially precharged in the first cycle from an auxiliary Li source.

3.3.1. Balanced cell $(r = r_b)$

The capacity of the anode and cathode in the first charge can be expressed by:

$$Q_c^- = q_c^- m^- \text{ (mAh)} \tag{2}$$

$$Q_c^+ = q_c^+ m^+ \text{ (mAh)} \tag{3}$$

where q_c^-, q_c^+ are the respective specific mass capacities.

From the definition of $r = m^+/m^-$ and the condition for a balanced cell Eqs. (2) and (3) yield:

$$r_b = q_c^-/q_c^+ \tag{4}$$

In the first discharge the capacity balance is offset on account of the difference in the coulombic efficiencies of the two electrodes, $(CE)_1^-$ and $(CE)_1^+$.

Assuming for convenience that $m^- = 1$ g and using Eqs. (2)–(4), the discharge capacities in the first cycle will be equal to:

$$Q_d^- = q_c^- (CE)_1^- \text{ (mAh)} \tag{5}$$

$$Q_d^+ = q_c^+ (CE)_1^+ r_b \text{ (mAh)} \tag{6}$$

When the merits of different electrode pairs, candidates for Li-ion cells, are considered it is necessary to know the specific volumetric capacity of the pair. For this purpose one should first calculate the volume of the pair, comprising the volume of the pressed electrodes with the inactive ingredients (conductive material and binder) but excluding the current collectors. From the apparent densities of the pressed electrodes d^-, d^+ and the contents of the active materials in each of them, a^-, a^+, the volume of the electrode pair is estimated by:

$$V_p = V^- + V^+ = 1/(d^- a^-) + r_b/(d^+ a^+) \text{ (cm}^3) \tag{7}$$

from which the specific volumetric capacity of the pair in the first discharge will be:

$$q_v = Q_d^\pm/V_p \text{ (mAh/cm}^3) \tag{8}$$

where $Q_d^\pm$ is the discharge capacity of the limiting electrode in the first cycle.

The ratio

$$R_d = Q_c^-/Q_c^+ = (CE)_1^-/(CE)_1^+ \tag{9}$$

is an indication of which the electrodes is the limiting one and a measure for the cell disbalance as well. This disbalance will, of course, change in the next five to ten cycles depending on the cycling stability of the electrodes. However, most cells are anode limited, implying that the anode is cycled at 100% depth-of-discharge (DOD), while the DOD of the cathode is quite lower.

Table 2
Description of the electrode pairs

Pair no.	Anode	Cathode	Electrolyte	Refs.
1	PFA-C	$LiCoO_2$	1 M $LiPF_6$, PC + DEC	[2]
2	Petroleum coke	$LiMn_2O_4$	1 M $LiClO_4$, PC + DEE	[10,22]
3	Petroleum coke	$LiNiO_2$	1 M $LiPF_6$, EC + DMC	This paper, [6–8]
4	Natural graphite	$LiNiO_2$	1 M $LiPF_6$, EC + DMC	This paper
5	Natural graphite	$LiNiO_2$	1 M $LiPF_6$, EC + DMC	[16]

Table 2 describes several electrode pairs already explored in Li-ion cells, while Table 3 presents their q_v values, calculated by Eqs. (2)–(9) using experimental data of q_c^+, q_c^-, $(CE)_1^-$ and $(CE)_1^+$ from recent literature data or from our experimental results. The values of $d^- = 1.50$ g/cm³, $d^+ = 2.4$ g/cm³, $a^- = 0.95$ and $a^+ = 0.85$ are assumed to be the same for all pairs for a more correct comparison. Table 3 also presents the initial parameters used in the calculation.

The q_v value of electrode pair 3 (Table 2) was checked experimentally in a balanced cell, $r_b = 1.66$, cycled between 2.6 and 4.3 V at 0.5 mA/cm². In the first cycle the charge capacities of the anode and cathode were very similar to those determined experimentally in two separate cells versus an Li counter electrode, i.e. 366 and 229 mAh/g, respectively. The coulombic efficiency of the cell in the first cycle, 64%, is equal to that of the anode which is the limiting electrode. The q_v value of this cell obtained by dividing the discharge capacity of the cell in the first cycle by the volume of the electrode pair measured geometrically is 150 mAh/cm³, close to that estimated in Table 2 for electrode pair 3. A good agreement between estimated and experimental q_v value was also obtained for the balanced electrode pair 4, $(q_v)_{exp} = 199$ mAh/g.

As a second check, the q_v value of the Sony's US-61-2060 Li-ion cell was calculated on the basis of the data revealed in Ref. [23], namely: 10 g active cathode material $LiCoO_2$, anode surface area = 228 cm², cathode surface area = 256 cm², and the data reported in Ref. [2] for the electrode capacities in the first cycle: charge 450 mAh/g for the anode and 146 mAh/g for the cathode, and discharge 320 mAh/g for the anode and 140 mAh/g for the cathode. In this calculation we assume that $a^+ = 0.85$, $a^- = 0.95$, $d^- = 2.40$ g/cm² and $d^- = 1.5$ g/cm³. The estimated value of $q_v = 150$ mAh/cm³ is almost equal to that calculated by Eqs. (2)–(9), pair 1 in Table 2.

The q_v data of several electrode pairs together with the capacity characteristics of the anodes and cathodes included in the pairs, shown in Table 3, make it possible to assess the relative contributions of the specific capacity, coulombic efficiency and density of each electrode on the value of q_v. Thus, for example by raising the cathode charging capacity in the first cycle by 51% without changing that of the anode (c.f. pairs 1 and 4) the q_v of the pair is raised by 39%. On the other hand, the increase in the initial charge anode capacity by only 24% of the same initial charge capacity (c.f. pairs 3 and 4) brings about a 33% increase in q_v of the pair. This demonstrates the importance of the efforts to increase the initial charge anode capacity where each 1% increase brings about 1.4% increase in q_v, while the same increase in the initial charge cathode capacity raises q_v by only 0.76%. It is also evident that the increase in the anode coulombic efficiency in the first cycle by 7% can raise the q_v of the pair with the same cathode by 13% despite the lower discharge initial capacity of the anode (c.f. pairs 4 and 5).

It should be noted that the specific capacities of the cathodes in the first discharge, q_d^+, in Table 3, are lower than those determined by Eq. (5), since the cell capacity is anode limited so that:

$$q_d^+ = Q_d^+ R_d / r_b = Q_d^- / r_b \qquad (10)$$

Eq. (10) indicates that the DOD of the cathode in the first cycle is equal to R_d.

The charge/discharge voltage profiles of a typical petroleum coke/1 M $LiClO_4$, EC + PC/$LiNiO_2$ nearly balanced cell, $r = 1.7$, in the seventh cycle between 4.25 and 2.6 V at 0.5 mA/cm² are shown in Fig. 7, curve (a). The potential profiles of the anode and cathode versus Li reference electrode are depicted by curves (b) and (c), respectively.
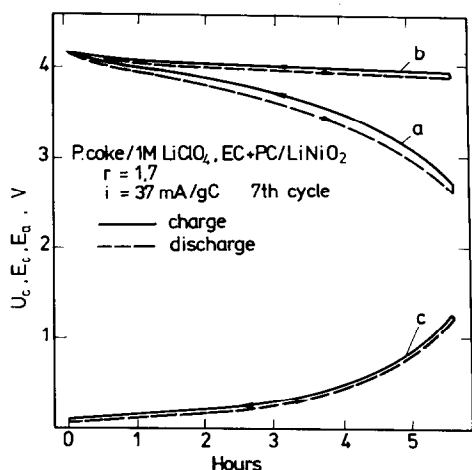
Table 3
Calculated volumetric specific capacities, q_v, of various electrode pairs in balanced cells and the experimental data used in the calculation

Pair no.	q_c^- (mAh/g)	q_c^+ (mAh/g)	r_b	$(CE)_1^-$ (%)	$(CE)_1^+$ (%)	Q_d^- (mAh)	Q_d^+ (mAh)	q_d^+ (mAh/g)	V_p (cm³)	R_d	q_v (mAh/cm³)
1	450	146	3.08	72	96	324	432	105	2.21	0.75	147
2	250	132	1.89	77	90	193	225	102	1.63	0.86	118
3	364	220	1.65	64	87	233	316	147	1.50	0.73	153
4	450	220	2.05	77	87	347	392	170	1.70	0.89	204
5	400	220	1.82	84	87	337	392	185	1.59	0.97	212

Fig. 7. Charge/discharge voltage profiles of a petroleum coke/LiClO$_4$, EC + PC/LiNiO$_2$ cell cycled between 2.60 and 4.25 V at 0.5 mA/cm^2: (a) cell voltage; (b) potential profiles of the cathode, and (c) potential profiles of the anode.
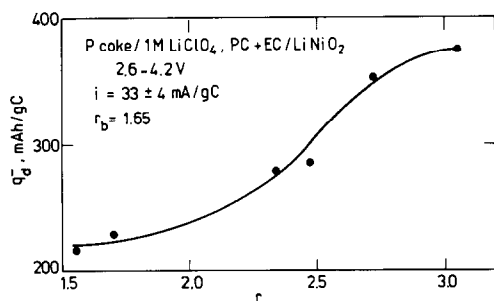

Fig. 8. Effect of r on the discharge capacity of the anode in petroleum coke/LiClO$_4$, EC + PC/LiNiO$_2$ cells cycled between 2.60 and 4.25 V at 0.5 mA/cm^2.
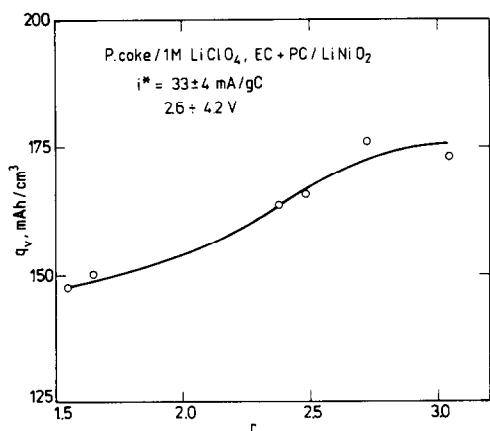

Fig. 9. Effect of r on the q_v value of petroleum coke/LiClO$_4$, PC + EC/LiNiO$_2$ cells.

3.3.2. Unbalanced cells with overcharged anode ($r > r_b$)

When $r > r_b$, the anode will be overcharged and in accordance with Eqs. (5) and (6) Q_d^-, Q_d^+, and q_v will be raised. In these cases the data in Table 2 are not valid and q_v should be found experimentally. In order to determine the effect of r on q_v a series of petroleum coke/1 M LiClO$_4$, EC + PC/

LiNiO$_2$ cells with $r > r_b$ were tested and their q_v values determined by dividing the discharge capacity of the cell in the first cycle by the geometrically measured volume of the electrode pairs. The cells were cycled under the same conditions: charge/discharge rate 6 ± 1 h, voltage limits, 2.60–4.25 V, temperature 25 ± 3 °C, water content in the electrolyte less than 30 ppm. As shown in Fig. 8, the increase in r from 1.8 to 3.1 raises the capacity of the anode in the first discharge by ~70%. The increase in q_v with r is not so strong, only ~16% (Fig. 9) since the volume of the electrode pair grows considerably with r (Eq. 7).

The overcharge of a petroleum coke/1 M LiClO$_4$, EC + PC/LiNiO$_2$ cell with $r = 2.72$ is illustrated by the voltage profiles of the first and sixth cycles in Fig. 10. In the first charging, curve (a) after the absorption of a capacity of 400 mAh/g, the anode potential becomes negative about -10 mV versus Li reference electrode. The final charge capacity is 600 mAh/g, i.e. the anode is with 180 mAh/g larger than that of an anode charged normally to 0 V. The anode coulombic efficiency in the first cycle, 58%, is raised up to 99.5% in the sixth, where the discharge capacity is 300 mAh/g
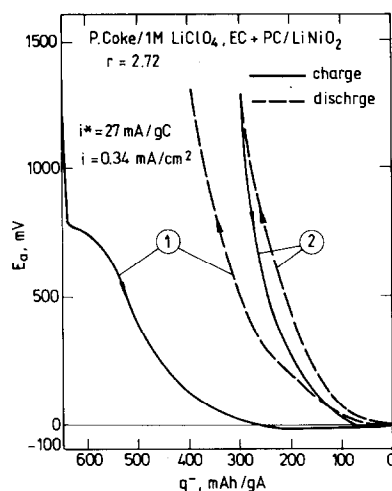

Fig. 10. Voltage profiles of the anode in a petroleum coke/LiClO$_4$, PC + EC/LiNiO$_2$ cell with $r = 2.72$ in the first and sixth cycles between 2.6 and 4.25 V at 0.5 mA/cm^2.
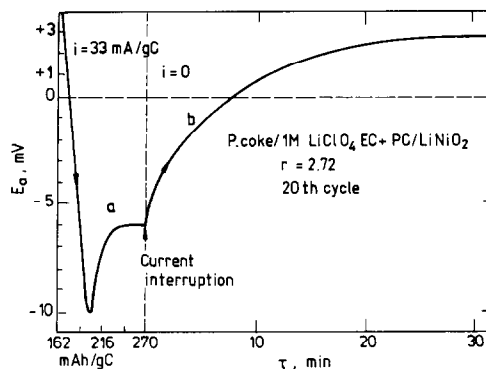

Fig. 11. Voltage profile of the anode in the cell in Fig. 10 at the end of the 20th charge: (a) before current interruption, and (b) after current interruption.
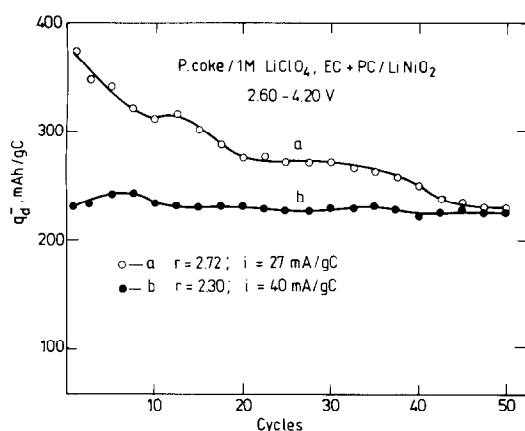
Fig. 12. Cycling test of two petroleum coke/LiClO₄, PC + EC/LiNiO₂ cells with different *r* values: (a) *r* = 2.72, and (b) *r* = 2.30.

(Fig. 10(b)). The final stage during the charging of this cell in the 20th cycle is presented in Fig. 11. After consumption of 190 mAh/g the anode potential has reached the 0 V level, whereafter it shifts in negative direction and reaches a minimum at − 10 mV within 1 h. The direction of the voltage shift is then reversed and at the end of the charge reaches − 6 mV. Here the current was interrupted and the open-circuit potential (OCP) of the anode was recorded at a higher chart speed (Fig. 11(b)). Within about 30 min the potential was established at + 3 mV.

The cathodic overvoltage of the anode after 190 mAh/g of charge (Fig. 11(a)) could be associated with the appearance of a new phase on the anode surface: either metallic Li or the first stage Li_xC_6 phase. The OCP of + 3 mV established after the current interruption cannot serve with certainty as an evidence for any of these two phases.

In spite of this overcharge of the anode, this cell, as shown in Fig. 12(a) was cycled 50 times without any sign of dendritic shorts and with an acceptable mean cycling stability, $CS = 99.2\%$. In contrast, as revealed in Fig. 12(b), the capacity retention on cycling of a similar cell but with $r = 2.30$ is much better, $CS = 99.8\%$, although the cell was cycled at a higher current density than the cell corresponding to Fig. 12(a). These results suggest that a moderate overcharge expressed by the ratio $r/r_b = 2.3/1.65 = 1.39$ provides a good cycling stability, while a strong one $r/r_b = 2.72/1.65 = 1.65$ is detrimental in the course of cycling.

If it is assumed that the anode is overcharged without the deposition of metallic Li, the above results may be explained by exfoliation of the coke lamellas, as suggested by Fong et al. [7]. On the other hand, if the overcharge results in the deposition of Li, the reduced cycling stability could be assigned to the presence of metallic Li. Preliminary a.c. impedance measurements of fully charged ($Li_{0.6}C_6$) and overcharged ($Li_{0.8}C_6$) coke anodes revealed considerably higher charge-transfer resistance and a lower double-layer capacitance compared with those of metallic Li in the same electrolyte, suggesting a different energy state of the Li ions on the surface of the overcharged coke anode.

3.3.3. Unbalanced cell with precharged anode ($r < r_b$)

This case was realized by Ohzuku et al. [24] by partially precharging the graphite anode with an auxiliary Li electrode. From the experimental data reported by these authors for the cell with a natural graphite anode and an LiNiO₂ cathode and using the previously assumed values of a^+, a^-, d^+ and d^-, it was possible to estimate the q_v of the electrode pair, 152 mAh/cm³, which is considerably lower than that for a balanced cell with the same electrode pair, 204 mAh/cm³ (Table 3, pair 4). This is due to the excess of the anode material, cycled at ∼ 200 mAh/g, i.e. at a DOD of ∼ 64%. This result and the need for an auxiliary Li anode make this type of cells rather impractical.

4. Cycling stability of petroleum coke/LiNiO₂ cell

The capacity decay of the petroleum coke/LiNiO₂ cells in the first five to ten cycles is usually considerable and reflects the initial capacity decay of the limiting electrode. Since the balanced and the moderately unbalanced cells with $r/r_b = 1.39$ are anode limited the initial capacity decay is governed by that of the anode. As shown by Fig. 3(a), the initial capacity decay of the petroleum coke in the first ten cycles is ∼ 6%. After the tenth cycle, however, the anode capacity is stabilized and its cycling stability reaches 99.83% (Section 1). On the other hand, the cycling stability of the cathode is higher, 99.90% (Section 2), so that its capacity decay could not affect that of the cell, even if during the cycling the cell became cathode limited. These considerations are corroborated by the results of the cycling test of a cell corresponding to Fig. 12(b) with $r/r_b = 1.39$, whose cycling stability determined after 50 cycles is equal to that of the anode $CS = 99.83\%$.

These findings clearly demonstrate that the cycling stability of the Li-ion cell is governed by that of the petroleum coke anode, so efforts should be made to improve $(CS)^-$ by looking for new carbonaceous materials and new anode formulations.

5. Conclusions

Li-ion cells are rapidly improving and each year new electrode materials are developed. The principal goal of these investigations is to increase the energy density of the cells. This determines the importance of the volumetric specific capacity of the electrode pairs, q_v, used in Li-ion cells. It appears obvious that for a given pair the maximum capacity will be achieved in a balanced cell. The equations proposed in this paper make it possible to calculate q_v for any electrode pair in a balanced Li-ion cell. The comparison between the q_v values of five pairs already explored in well-investigated Li-ion cells could suggest the most efficient way for a further increase in cell capacity. It is shown that by increasing the capacity of the anode the capacity of the pair will be raised

twice as much in percents than by increasing the capacity of the cathode. A good agreement between calculated and experimental q_v values is found. The influence of the material balance ratio, r, on the cycling stability and the possibility of using unbalanced cells with moderately overcharged anodes are demonstrated with the example of the petroleum coke/ $LiNiO_2$ cell.

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