

State of the art of commercial Li ion batteries

R. Moshtev^{a,*}, B. Johnson^b

^a Department of Lithium Systems Electrochemistry, Central Laboratory of Electrochemical Power Sources, Bulgarian Academy of Sciences (BAS), Sofia 1113, Bulgaria

^b In Genius, 6575 Industrial Way, Alpharetta, GA 30004, USA

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Abstract

A number of criterial specific parameters of the electrodes in five commercial Li ion batteries of leading producers are derived on the basis of the recently published data by Johnson and White [B.A. Johnson, R.E. White, J. Power Sources 70 (1998) 48]. The impact of these parameters on the cycling performance of the cells is analyzed. It is shown that in spite of the similarities in the type of the electrode, electrolyte and separator materials, there are considerable differences in the capacity, masses, apparent densities and material balance ratio. For example the A&T cell with the smallest masses of its active electrode materials and lowest apparent densities of the electrodes has achieved the largest cell capacity, highest rate capability and cycling stability. This is accomplished thanks to the high quality of its electrode materials' novel electrode design with double current collectors for each electrode and largest material balance ratio. The above and other examples in the paper reveal the complexity of interactions between the criterial parameters of the electrodes and indicate that an improvement in the cell performance requires not only investigations but creativity as well. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Commercial Li ion batteries; LiCoO₂ cathode; Accumulated capacity; Ragone plots; Polarization resistance

1. Introduction

The introduction of the Sony rechargeable Li ion battery in 1991 marks the beginning of a period of development of a new generation of small-size high-energy sources. The lithium metal-free batteries with carbonaceous anodes, lithiated oxides of transition metals of the 3d group as cathodes, as well as ethylene carbonate-based electrolytes are characterized not only with high energy density, high rate capability, long cycle life, but what is most important is its large degree of safety. All these distinctions of the new batteries and the rapidly increasing demand of small batteries by the portable telecommunication and computer market led to an unprecedented increase in their production. Presently, more than 10 Japanese, American, European and Asian companies are fabricating annually tens of millions.

The recently published detailed description by Johnson and White [1] of the materials, design, physical properties,

electrochemical parameters and cycling performance of five commercially available Li ion cells revealed many similarities between them, e.g., same cathode material (LiCoO₂), similar anode materials (graphite or coke), similar electrolytes based on LiPF₆ and ethylene carbonate, same current collector foils, similar separator materials, same jelly roll configuration and same size.

Nonetheless, there are quite many differences in some of the physical parameters and the performance characteristics of the cells with respect to capacity, rate capability, cycling stability accumulated capacity and cell resistance. It would be of interest both for the cell designers and the scientists involved in the investigation of electrode materials to elucidate as far as possible the effect of some of the physical and electrochemical characteristics of the electrodes and of the cell design on these performance parameters.

Based on the data disclosed in Ref. [1], a number of specific physical and electrochemical relationships are derived in this paper which exerts more influence on the cell performance than others. Their knowledge could be helpful in the efforts for the optimization of the batteries and the materials they use.

* Corresponding author. Tel.: +359-2-709-388; fax: +359-2-722-544.

Table 1
Physical characteristics of the commercial Li ion batteries and of their electrodes

Characteristics	Sony	Moli	A & T	Sanyo	Matsushita	Average	References
<i>Cell</i>							
Total mass, g	39.4	41.9	40.8	38.1	(24.1)	40.0	[1]
Packaging density, %	77	78	(56)	76	(1.18)	78	–
Material balance ratio, r	3.41	1.61	3.83	1.57	(1.18)	–	–
Volume of electrode pair, cm ³	8.68	9.65	7.17	8.04	(5.08)	–	–
<i>Positive, LiCoO₂</i>							
Mass of electrode material, g	13.6	12.5	10.6	11.3	(6.2)	–	[1]
Mass of LiCoO ₂ , g	11.6	10.6	9.2	9.6	(5.3)	–	–
Geometric area (both sides), cm ²	493	532	(422)	498	(254)	–	[1]
Loading (one side), mg/cm ²	23.5	19.9	21	19.3	20.9	20.9	–
Thickness, μm	160	153	(94)	155	160	157	[1]
Electrode volume, cm ³	3.94	4.07	3.97	3.86	(2.03)	3.91	–
Apparent density, g/cm ³	3.45	3.07	2.68	2.93	3.05	3.13	–
Porosity, %	(26.8)	34.8	43.3	37.8	35.2	–	–
<i>Negative, Li_xC₆</i>							
Mass of electrode material, g	(3.5)	6.9	(2.5)	6.4	(4.7)	6.7	[1]
Mass of carbon material, g	3.4	6.6	(2.4)	6.1	(4.5)	6.4	–
Geometric area (both sides), cm ²	542	603	(421)	577	(308)	–	[1]
Loading, mg/cm ²	12.2	10.9	(5.7)	10.6	14.6	12.1	–
Thickness, μm	175	185	(76)	(145)	198	186	[1]
Electrode volume, cm ³	4.74	5.58	(3.20)	4.18	(3.05)	–	–
Apparent density, g/cm ³	(0.74)	(1.24)	(0.78)	1.53	1.54	–	–
Porosity, %	64.8	41.0	62.9	27.1	26.7	–	–

Table 1 presents the most significant physical characteristics of the cells as disclosed in Ref. [1], as well as some additional parameters derived from them such as packaging density, material balance ratio, volume of electrode materials, loading, apparent density of electrodes and their porosity. In the estimation of the average values of these characteristics (where reasonable) the bracketed values are omitted either because of the different design as in the A & T cell or of different size, as in Matsushita. Some extreme values are also omitted. The masses of the elec-

trodes comprise the active and conductive materials and binders. The volumes of the electrodes comprise the volumes of the same materials plus that of the pores. The masses of the pure active materials m^+ and m^- are estimated from those of the electrode materials assuming that the relative active mass content is 85% for the positive and 95% for the negative. In all cells, the same current collectors are used: 25 μm Al foil for the positive and 18 μm Cu foil for the negative. In four of the cells, the electrode material is applied on both sides of the foils,

Table 2
Cycling conditions of the cells and electrodes

Cycling conditions	Sony	Moli	A & T	Sanyo	Matsushita	Average	References
<i>Cell</i>							
Charging potential limit, V	4.2	4.2	4.2	4.2	4.2	–	[1]
Charging current limit, A	1.0	1.0	1.0	1.0	0.5	–	[1]
Discharge current at $C/5$, mA	236	260	290	260	164	–	–
<i>Positive, LiCoO₂</i>							
Charging current limit, mA/g	86	94	(109)	104	94	95	–
Charging current limit, mA/cm ²	2.03	1.88	(2.37)	2.61	1.97	1.97	–
Discharge current at $C/5$, mA/g	20.3	24.5	(31.5)	27.1	30.9	25.7	–
Discharge current at $C/5$, mA/cm ²	0.48	0.49	(0.69)	0.52	0.65	0.49	–
<i>Negative, Li_xC₆</i>							
Charging current limit, mA/g	(294)	152	(417)	164	(111)	–	–
Charging current limit, mA/cm ²	1.85	1.66	(2.38)	1.73	1.62	1.72	–
Discharge current at $C/5$, mA/g	(69.4)	39.4	(121)	42.6	36.4	–	–
Discharge current at $C/5$, mA/cm ²	0.44	0.43	(0.69)	0.45	0.53	0.46	–

Table 3
Performance data of the batteries and their electrodes

Performance data	Sony	Moli	A&T	Sanyo	Matsushita	References
<i>Cell</i>						
Discharge capacity at $C/5$, A h	1.18	1.30	1.45	1.30	0.82	[1]
Mid-discharge voltage, V	3.50	3.75	3.75	3.75	3.75	[1]
Volumetric capacity, mA h/cm ³	71.3	78.6	87.7	78.6	72.2	–
Gravimetric capacity, mA h/g	30.0	31.0	35.6	34.1	34.0	–
Energy density, W h/l	250	295	329	295	271	–
Energy density, W h/kg	105	116	134	128	128	–
Accumulated capacity after 500 cycles at $C/2$, A h	576	471	716	492	324	–
Capacity loss after 500 cycles, %	12.3	50.0	15.7	40.5	9.5	–
Capacity drop between $C/5$ and $3C$ rate, %	81.9	93.3	7.8	59.6	7.6	–
Polarization resistance at rates above $1C$, Ω cm ²	213	189	54	118	50	–
<i>Positive, LiCoO₂</i>						
Gravimetric capacity, mA h/g	102	123	158	135	155	
Volumetric capacity, mA h/cm ³	299	319	365	337	402	
<i>Negative, Li, C₆</i>						
Gravimetric capacity, mA h/g	358	197	604	213	182	
Volumetric capacity, mA h/cm ³	250	233	453	311	269	
<i>Electrode pair</i>						
Volumetric capacity, mA h/cm ³	136	135	202	162	161	

whereas in the A&T cell, there are two foils for each electrode with the electrode material applied on one side only. The loading is calculated by dividing the mass of the active material by its geometric area. The electrode volumes are obtained by multiplying the electrode thickness by its geometric area divided by two except for that of the A&T cell, where the area shown is not divided. Four of the cells are of the 18650 size that indicates their diameter is 18 mm and length is 65 mm. Only the Matsushita cell is of the 17500 size, i.e., 17 mm in diameter and 50 mm long. The packaging density is estimated according to Eq. (4). Table 2 describes the cycling conditions of the cells. Here, the gravimetric capacities are with respect to the mass of the pure active material only. The charging voltage limit is 4.2 V and the discharge cut-off voltage is 2.5 V for all cells. Table 3 gives the performance characteristics of the electrodes and the cells. The specific capacities and energies of the cells are with respect to total cell mass or volume, which is 11.35 cm³ for the Matsushita cell and 16.54 cm³ for the four other cells.

It is noteworthy that the data reported by Johnson and White [1] are based on the results obtained from testing of 85 cells of the five manufacturers.

2. Discussion

2.1. Effect of packaging density and porosity

The gravimetric discharge capacity, q_d , of each of the electrodes, determined at the given cycling conditions is equal to

$$q_d = \eta q_r, \text{ A h/g} \quad (1)$$

where η is the utilization coefficient, called further utilization for brevity, and q_r is the reversible discharge capacity determined at sufficiently low rates (to avoid the influence of diffusion hindrances) and in a voltage range providing simultaneously large capacity, stable cyclability and safety of the cell. The value of η is dependent on many other factors such as temperature, load, chemistry of the intercalation compounds used for the electrodes, composition of the electrolyte, material balance ratio, and by the thickness and porosity of the electrodes.

Since as a rule the capacity, Q , of a Li ion cell is often limited by that of the anode, Q^- , we can write

$$Q = Q^- = m^- q_d^-, \text{ A h} \quad (2)$$

where q_d^- and m^- refer to the discharge capacity and mass of the active anode material. A similar equation is valid also for the positive. Inasmuch as the volume available for the electrode materials is a basic limiting factor it is more convenient to use expression (3)

$$Q = Q^- = q_d^- d_{ap}^- V^- a^-, \text{ A h} \quad (3)$$

with d_{ap} as the apparent density of the anode, V^- as its volume and a^- as the relative mass content of the pure active material in the anode mixture.

Another important characteristics of the cell design, significantly affecting its capacity is the packaging density, p . It was defined by Atlung et al. [2] as the ratio of the mass of the active materials to the total battery mass. It is clear that the larger the value of p , the larger the effectiveness of the cell design and, for cells of similar size and chemistry, this means a larger capacity. For the small-size,

volume-limited Li ion batteries, it appears more rational to introduce a volumetric packaging density of the cell roll, neglecting the volumes of all parts of the casing, header and voids, taking into account that they are approximately similar for cells of the same size. The volumetric packaging density, p , is expressed here as

$$p = (V^+ + V^-) / (V^+ + V^- + V_s + V_{cc}) \quad (4)$$

where V^+ and V^- are the volumes of the electrode materials including additives and pores and V_s and V_{cc} are the volumes of the separators and the current collectors. For a given geometric area of the electrodes, p , can be expressed also as

$$p = (l^+ + l^-) / (l^+ + l^- + l_s + l_{cc}) \quad (4')$$

with l as the respective thickness.

As seen in Table 1, the p values of four of the cells are quite similar ($78 \pm 1\%$). The considerably lower $p = 56\%$ of the A&T cell reflects its special electrode design and one should expect that this could bring about a lower cell capacity. As shown in the same Table 1, however, the capacity of this cell is noticeably larger than that of the other four cells.

The apparent density of the electrodes is also an important physical characteristics (see Table 1). The latter is determined by dividing the total mass of the electrode, m_e , (including the active mass and the additives) by its volume, V , including the pore volume.

$$d_{ap} = m_e / V, \text{ g/cm}^3 \quad (5)$$

The volumetric porosity of the electrode, π , is the ratio of the pore volume to that of the electrode and is calculated by

$$(100 - \pi) = d_{ap} / d_t \times 100, \% \quad (6)$$

where d_t is the true density of the electrode.

It is well established, both theoretically [2] and experimentally, that for a porous electrode with a given chemistry, thickness and the same relative mass content of the active material in the electrode material, a , the increase in the porosity, π , leads to the enhancement of the utilization and, respectively, of the gravimetric discharge capacity in the electrode, q_d . However, according to Eq. (6), this brings about the reduction of the apparent density, d_{ap} , whereby as shown by Eq. (3) the cell capacity could diminish above a certain value of π . The influence of π^+ on the gravimetric capacity of the cathodes of four of the commercial cell with the same size, the same cathode material, similar thickness (Table 1) and the same value of $a^+ = 0.85$ is illustrated by the two plots in Fig. 1, pertaining to two discharge rates, $C/5$ and C . The steep rise of q_d^+ with π^+ explains that the large capacity of the A&T cathode is basically due to its high porosity. No similar dependence can be obtained for the anodes in view of the

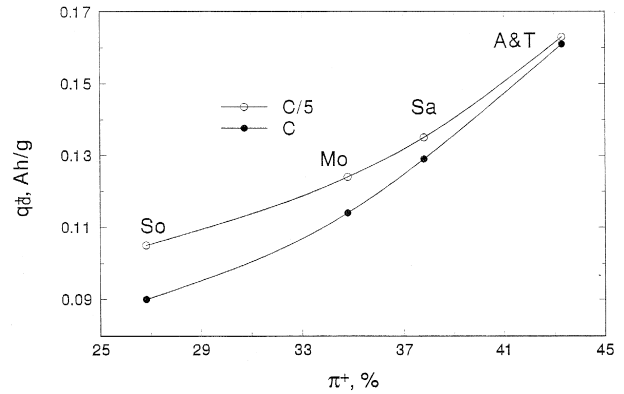


Fig. 1. Effect of porosity π^+ on the gravimetric capacity of the cathodes of the four commercial batteries of size 18650 at two rates: $C/5$ and C .

considerable difference in the nature of the carbonaceous materials employed.

2.2. Material balance ratio

The characteristics of the cathode which is usually not capacity limiting, are not less important for the cell performance. Its capacity and, respectively, its mass and volume should be large enough as to supply the amount of Li^+ ions necessary to charge the anode to a potential close to that of Li. This requirement is regulated by the material balance ratio r introduced by Guyomard and Tarascon [3], $r = m^+ / m^-$.

For the maximum utilization of the electrode materials, the cell should be balanced so that in the first cycle, the charge capacity of the cathode should be equal to that of the anode or that $r = r_b$ which is expressed by

$$Q_{c1}^- = Q_{c1}^+ \quad (7)$$

or by

$$q_{c1}^- m^- = q_{c1}^+ m^+ \quad (8)$$

and from the definition of r it follows

$$r_b = (q_{c1}^- / q_{c1}^+) \quad (9)$$

where q_{c1}^- and q_{c1}^+ are the gravimetric charge capacities of the electrodes in the first cycle. Alternatively, r_b can be expressed by the respective discharge capacities, q_d

$$r_b = (q_{d1}^- / q_{d1}^+) (\eta_1^- / \eta_1^+) \quad (10)$$

where (η_1^- / η_1^+) is the ratio between the utilization coefficients of the anode and the cathode in the first cycle. The effect of r on the performance of a petroleum coke/LiNiO₂ cell was reported in Ref. [4]. It was shown that in a cell with $r/r_b > 1$, the anode is overcharged with the risk that metallic Li will be deposited on its surface, whereby its safety is endangered. Parallel with this the carbon layers of the anode material can be split and its cycling stability impaired. In the opposite case, if $r/r_b < 1$, the anode will

remain incompletely charged which will result in a lower cell capacity and discharge voltage.

On the other hand, the requirements for safety and longevity impose the condition that r/r_b should be somewhat lower than unity. Practically, it is hardly possible to estimate in advance the optimum r value because r_b is dependent on the values of η^- and η^+ , which in turn are functions of load and temperature.

Unfortunately, there are no data in Ref. [1] necessary to estimate r_b and, respectively, r/r_b of the five batteries. The large differences of their r values (Table 1) reflect basically the variances in their specific anode capacities and, respectively, the different types of carbonaceous materials used for their anodes.

2.3. Effect of alternative cathode materials

It is well recognized that the widely used LiCoO_2 in the commercial Li ion batteries is in competition with other 4-V cathode materials and more specifically with LiNiO_2 and LiMn_2O_4 . For the battery engineers, it would be of interest to evaluate in advance the expected capacities of the five commercial cells if these two alternative cathode materials are introduced instead of LiCoO_2 , by preserving the same anodes and the same volumes of the electrode pairs, V_p . For this purpose, it was first necessary to calculate the volumetric capacities of the cathodes. Those of the cells with LiCoO_2 were obtained directly by Eq. (11) (Table 3).

$$q_v^+ = Q/V^+, \text{ Ah/cm}^3 \quad (11)$$

In the case of the cells with alternative cathode, where Q has to be calculated, the values of q_v^+ can be determined by Eq. (12).

$$q_v^+ = q_m^+ d_{ap}^+ a^+, \text{ Ah/cm}^3 \quad (12)$$

Here q_m^+ is the gravimetric discharge capacity of the cathode and $a^+ = 0.85$ is as previously assumed. The apparent density of the cathode, d_{ap}^+ , can be calculated by Eq. (6), where the true density of the cathode material d_t^+ (excluding the volume of the pores) is given by Eq. (13).

$$d_t^+ = (0.85d_{am}^+ + 0.15d_{ad}^+), \text{ g/cm}^3 \quad (13)$$

Here d_{am}^+ is the density of the pure active material: 5.17 g/cm^3 for LiCoO_2 , 4.71 g/cm^3 for LiNiO_2 , and 4.28 g/cm^3 for LiMn_2O_4 . The density of the additives (conduc-

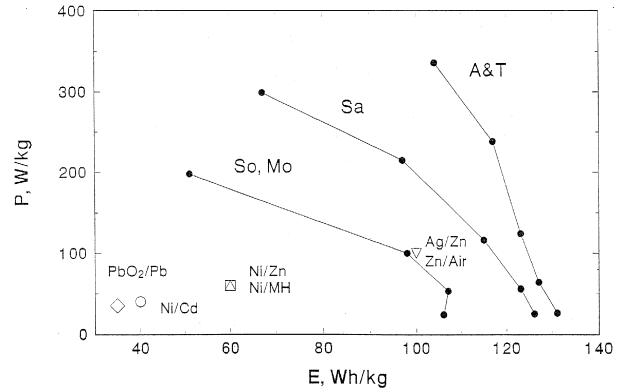


Fig. 2. Linear Ragone plots of the four commercial batteries of size 18650.

tive and binding materials), d_{ad}^+ is usually accepted as 2.1 g/cm^3 . For the calculation of d_{ap}^+ by Eq. (6), we have assumed here the high porosity of the A&T cathode of 43.3%. The values of d_{ap}^+ thus obtained are 2.46 g/cm^3 for LiNiO_2 and 2.26 g/cm^3 for LiMn_2O_4 . For the value of q_m^+ of LiNiO_2 , we assume here our recent experimental data [5] of 0.175 A h/g obtained at the $C/4$ rate after 20 cycles and for the LiMn_2O_4 cathode, the recent literature value of 0.120 A h/g . The volumetric capacities of these cathodes calculated by Eq. (12) are 0.366 A h/cm^3 for LiNiO_2 and 0.230 A h/cm^3 for LiMn_2O_4 . The volumetric capacity of the electrode pair $q_{v,p}$ was obtained by the well-known expression for two capacitors connected in series (14)

$$(q_{v,p})^{-1} = (q_v^+)^{-1} + (q_v^-)^{-1}, \text{ cm}^3/\text{Ah} \quad (14)$$

where q_v^- are the values for the anode of the respective commercial battery with a LiCoO_2 cathode (Table 3).

The expected capacities of the batteries with the alternative cathodes, Q_{ex} , will be then equal to

$$Q_{ex} = V_p q_{v,p}, \text{ Ah} \quad (15)$$

The calculation for the Li ion batteries with LiNiO_2 cathode reveals a small decrease of Q_{ex} with respect to the nominal ones with LiCoO_2 of -3% for the Matsushita cell, no change for the A&T cell and limited increases for the Sony, Moli and Sanyo cells of 9.2% , 7.1% , and 4.6% , respectively. For the batteries with the LiMn_2O_4 cathodes there is a considerable capacity reduction: -11.0% for Sony, -13.8% for Moli, -24.8% for A&T, -17.7% for Sanyo and -23.3% for Matsushita. The above figures cannot claim high accuracy but they clearly reveal the advantage of the Li ion batteries with LiCoO_2 and LiNiO_2 cathodes over those with LiMn_2O_4 cathodes.

It is noteworthy that the Q_{ex} values for the commercial batteries with the LiCoO_2 cathodes, estimated by the above procedure with Eqs. (6), (11)–(15) are exactly equal to their nominal cell capacities exhibited in Table 1.

Table 4
Accumulated capacity and capacity loss after 500 cycles at $C/2$ rate

Cell	A&T	Sony	Sanyo	Moli
Q_{ac} , A h	716	576	492	471
Loss, %	16	12	41	93

Table 5
Polarization resistance at mid-discharge

Cell	A&T	Matsushita	Sanyo	Moli	Sony
$R_p, \Omega \text{ cm}^2$	54	50	118	189	213

2.4. Accumulated discharge capacity

The accumulated discharge capacity during a long term cycling test reflects the initial high capacity of the cell as well as its cycling stability. The values of Q_{ac} shown in Table 4 were estimated by graphical integration of the plots reported by Johnson and White (Fig. 7, Ref. [1]) after 500 cycles at a $C/2$ rate. The data reveal that the A&T cell outperforms by 24% the next best cell of Sony. Table 4 presents also the relative capacity loss of the cells after 500 cycles. The low capacity losses of the Matsushita, Sony and A&T cells of 9.5%, 12.3% and 15.7% are quite remarkable. It should be pointed out, however, that the discharge current density of the anodes of the A&T cell at this rate is considerably larger, 302 mA/g, than those of the Matsushita and Sony cells, 91 and 174 mA/g. On the other extreme, the losses of the Sanyo and Moli cell are very high, 40.5% and 50.0%. These high values cannot be assigned to some poor design parameters but rather to lower quality electrode and electrolyte materials.

2.5. Power capability

The power capability of the four commercial batteries of the same size is demonstrated by their linear Ragone plots in Fig. 2. The plots clearly reveal the superiority of the A&T battery which at the $3C$ rate yields 340 W/kg with an energy loss of only 18% with respect to that at the nominal $C/5$ rate. The next best battery of Sanyo yields 300 W/kg but its energy loss is 67% compared to that at the nominal rate. Both batteries of Sony and Moli cannot operate at the $3C$ rate and their performance even at the $2C$ rate is considerably lower. Fig. 2 shows also, for the

sake of comparison, literature data of the most popular commercial rechargeable batteries obtained at the C rate. Both their power and energy are noticeably inferior to the Li ion batteries of A&T and Sanyo.

2.6. Polarization resistance

One of the main characteristics determining the power capability of the batteries is their polarization resistance, R_p . The latter comprises many components of ionic, electronic and diffusion character. The largest of these is normally associated with the slow diffusion of Li in the intercalation compounds used as active materials in both electrodes. The diffusion rate of Li in both electrodes is strongly dependent on their state of discharge so that a reasonable comparison should be made at the same state. The mid-discharge voltage obtained at a given current density is perhaps the best reference point in this respect. The galvanostatic discharge voltage profiles of the five commercial cells presented in the paper of Johnson and White [1] at five different rates were used to plot the mid-discharge voltages vs. the current density, referred to the geometric area of the cathodes. The R_p values obtained from the slopes of these plots at rates equal and higher than C , where the plots are linear as shown in Table 5. The remarkably low R_p of the A&T battery is evidently due to use of two current collectors for each electrode. The low R_p of the Matsushita battery is probably related to the shorter electrodes and possibly to the use of more tabs.

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