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Electrochemical Properties of Cathode $LiNi_{1-y}Tl_yO_2$ Synthesized by Milling and Solid-State Reaction Method

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Abstract: $LiNi_{1-y}Tl_yO_2$ (y = 0.005, 0.01, 0.025, 0.05 and 0.1) were synthesized by milling and solid-state method. Their electrochemical properties were then compared with those of $LiNi_{1-y}M_yO_2$ (M = Ga^{3+} and In^{3+}). All the samples had the $R\bar{3}m$ structure. $LiNi_{0.95}Tl_{0.05}O_2$ has the largest first discharge capacity 179.8 mAh g^{-1} and the discharge capacity 113.8 mAh g^{-1} at the 20th cycle. $LiNi_{0.995}Tl_{0.005}O_2$ has the smallest first discharge capacity 125.4 mAh g^{-1}. The samples exhibit similar cycling performances. $LiNi_{0.975}Ga_{0.025}O_2$ and $LiNi_{0.9}In_{0.1}O_2$ had the best electrochemical properties among the samples substituted by the same element, respectively. Among $LiNi_{0.975}Ga_{0.025}O_2$, $LiNi_{0.9}In_{0.1}O_2$ and $LiNi_{0.95}Tl_{0.05}O_2$, $LiNi_{0.95}Tl_{0.05}O_2$ has the largest first discharge capacity, but has the worst cycling performance. $LiNi_{0.975}Ga_{0.025}O_2$ has the smallest first discharge capacity, but has the smallest capacity degradation rate 0.70 mAh g^{-1} $cycle^{-1}$.

Key words: $LiNi_{1-y}Tl_yO_2$, milling, solid-state reaction method, electrochemical properties, I_{003}/I_{104}, R-factor

Introduction

The transition metal oxides such as $LiMn_2O_4$ (Tarascon *et al*., 1991; Armstrong and Bruce, 1996; Song and Ahn, 1998), $LiCoO_2$ (Ozawa, 1994; Alcatara *et al*., 1997; Peng *et al*., 1998) and $LiNiO_2$ (Dahn *et al*., 1990, 1991; Marini *et al*., 1991; Ebner *et al*., 1994) have been investigated in order to apply them to the cathode materials of lithium secondary battery. $LiMn_2O_4$ is very cheap and does not bring about environmental pollution, but its cycling performance is not good. $LiCoO_2$ has a large diffusivity and a high operating voltage and it can be easily prepared. However, it has a disadvantage that it contains an expensive element Co. $LiNiO_2$ is a very promising cathode material since it has a large discharge capacity (Nishida *et al*., 1997) and is relatively excellent from the view points of economics and environment. On the other hand, its preparation is very difficult as compared with $LiCoO_2$ and $LiMn_2O_4$.

It is known that $Li_{1-x}Ni_{1+x}O_2$ forms rather than stoichiometric $LiNiO_2$ during preparation. This phenomenon is called cation mixing. Excess nickel occupies the Li sites, destroying the ideally layered structure and preventing lithium ions from easy movement for intercalation and deintercalation during cycling. This results in a small discharge capacity and a poor cycling performance. To solve the problem of cation mixing, Co^{3+}, Al^{3+}, Mn^{3+} and Ti^{4+} ions were substituted for lithium ion in $LiNiO_2$

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(Gao *et al*., 1998; Kim and Amine, 2001; Broussely, 1999; Caurant *et al*., 1996; Zhang *et al*., 2004; Amriou *et al*., 2004; Shinova *et al*., 2005). According to Kim and Amine (2001, 2002) and Gao *et al*. (1998), the substitution of Ti for Ni resulted in a large discharge capacity and a good cycling performance.

In this study $LiNi_{1-y}Tl_yO_2$ (y = 0.005, 0.01, 0.025, 0.05 and 0.1) were synthesized by milling and solid-state method and the electrochemical properties of the synthesized samples were investigated. Their electrochemical properties were then compared with those of $LiNi_{1-y}M_yO_2$ ($M = Ga^{3+}$ and In^{3+}) synthesized by the same method in our earlier study (Kim *et al*., 2005a,b). The substituted Ga and In have the same oxidation number as Tl.

Materials and Methods

The $LiNi_{1-y}Tl_yO_2$ (y = 0.005, 0.01, 0.025, 0.05 and 0.1) are synthesized by milling and solid-state method under the optimum conditions for the preparation of $LiNiO_2$, previously studied (Kim *et al*., 2005). LiOH H_2O (Kojundo Chemical Lab. Co., Ltd, purity 99%), $Ni(OH)_2$ (Kojundo Chemical Lab. Co., Ltd, purity 99.9%), $TlNO_3$ (Aldrich Chemical, 99.9%) are used as starting materials. The starting materials are mechanically mixed by SPEX milling for 1 h. The mixed materials are preheated at 450°C for 5 h in air, then pressed into pellet and calcined at 750°C for 30 h under oxygen stream. The phase identification of the synthesized samples is carried out by X-ray powder diffraction analysis (Rigaku III/A diffractormeter) using Cu Kα radiation. The scanning rate is $6°min^{-1}$ and the scanning range of diffraction angle (2θ) is $10° \leq 2\theta \leq 80°$. The electrochemical cells consist of $LiNi_{1-y}Tl_yO_2$ as a positive electrode, Li foil as a negative electrode and electrolyte [Purelyte (Samsung General Chemicals Co., Ltd.)] prepared by solving 1M $LiPF_6$ in a 1:1 (volume ratio) mixture of Ethylene Carbonate (EC) and diethyl carbonate (DEC). The positive electrode consists of 85 wt.% synthesized materials, 10 wt.%

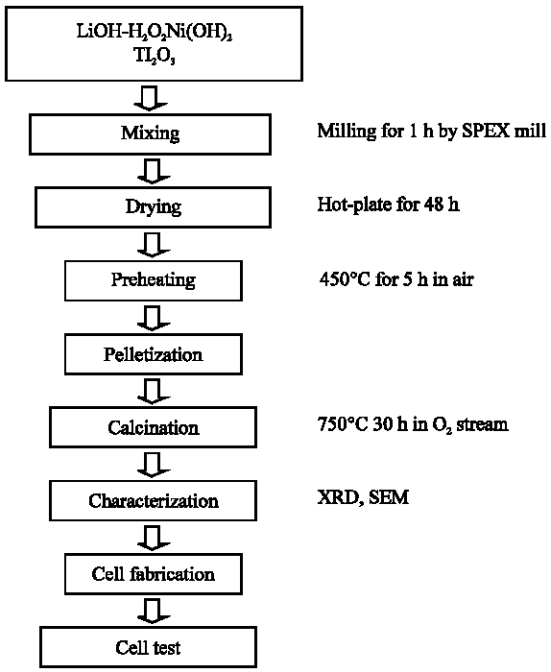


Fig. 1: Experimental procedure for $LiNi_{1-y}Tl_yO_2$ electrode prepared by solid-state reaction method after milling

acetylene black and 5 wt.% polyvinylidene fluoride (PVDF) binder solved in 1-Methyl-2-pyrrolidinone (NMP). A Whatman glass-filer is used as a separator. The cells are assembled in argon-filled dry box and the cell type is coin-type (2016). All the electrochemical tests are performed at room temperature with a potentiostatic/galvanostatic system. The cells are cycled between 2.7 and 4.2 V at 0.1 C-rate.

Figure 1 shows experimental procedure for the $LiNi_{1-y}Tl_yO_2$ electrodes prepared by milling and solid-state reaction method.

Results and Discussion

Figure 2 shows X-ray powder diffraction (XRD) patterns of $LiNi_{1-y}Tl_yO_2$ (y = 0.005, 0.01, 0.025, 0.05 and 0.01) calcined at 750°C for 30 h. All the samples have only the phase with $R\bar{3}m$ structure and do not exhibit the peaks of impurity. The $R\bar{3}m$ structure is distored in c-axis direction. This is reflected by the split of 006 and 102 peaks and of 108 and 110 peaks in the XRD patterns. The 108 and 110 peaks were split for all the samples.

It is generally known that the cation mixing is small if the intensity ratio of 003 peak to 104 peak (I_{003}/I_{104}) is large (Ohzuku *et al*., 1993). The value of $(I_{006}+I_{102})/I_{101}$, called R-factor, is known to be smaller when the hexagonal ordering is high (Dahn *et al*., 1990). In addition, the split between 108 and 110 peaks is reported to suggest the smaller cation mixing and the better hexagonal ordering (Ohzuku *et al*., 1993).

Table 1 gives the lattice parameters a, c, c/a, I_{003}/I_{104}, R-factor and unit cell volume calculated from XRD patterns of $LiNi_{1-y}Tl_yO_2$ (y = 0.005, 0.01, 0.025, 0.05 and 0.01) calcined at 750°C for 30 h. The sample with y = 0.005 has the largest I_{003}/I_{104} and all the samples have the smallest value of R-factor.

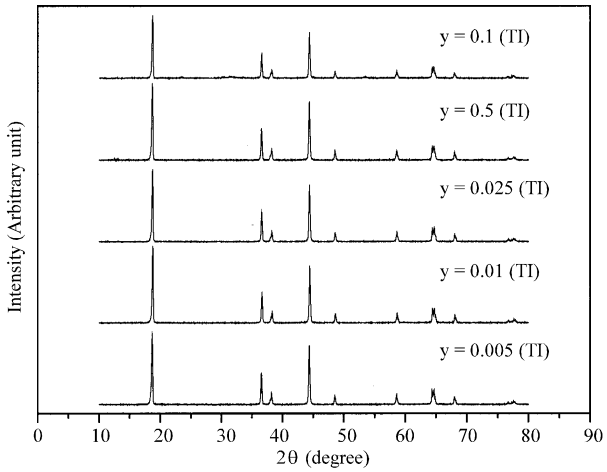
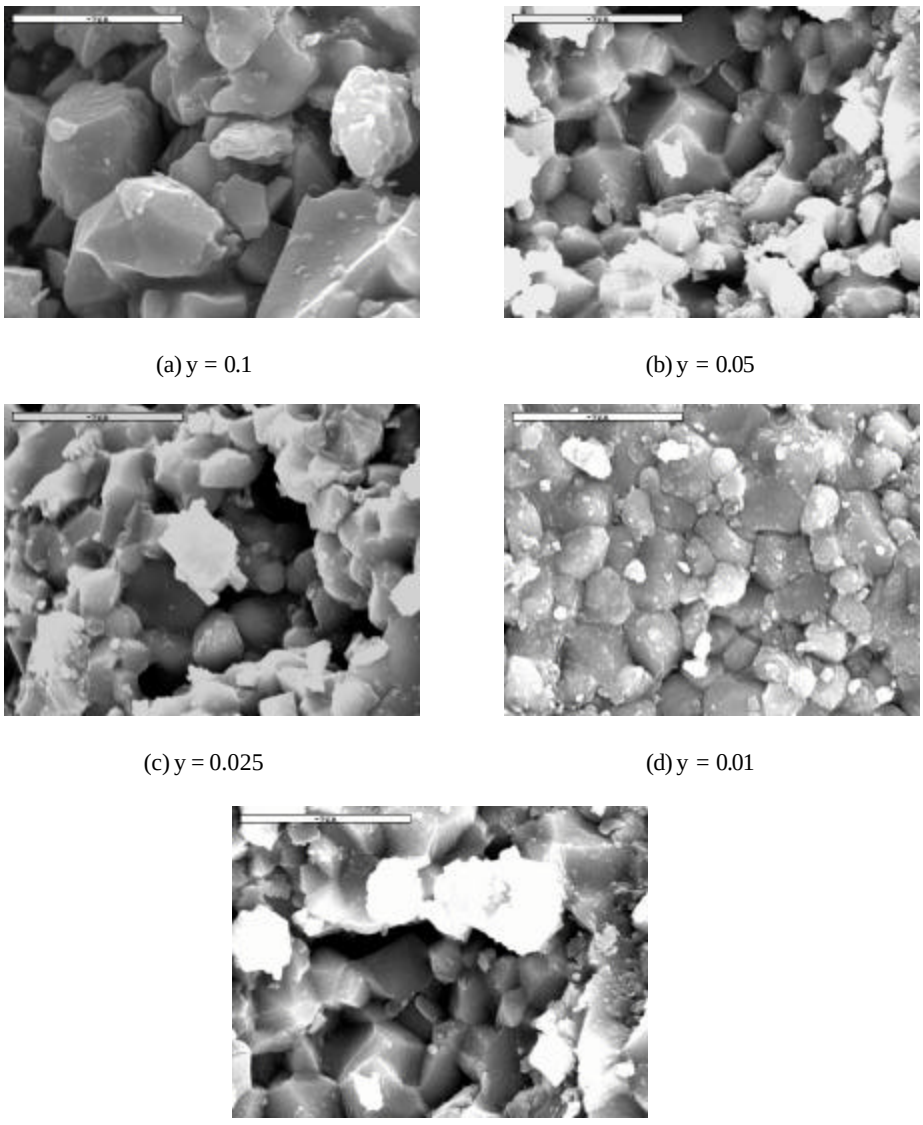


Fig. 2: XRD patterns of $LiNi_{1-y}Tl_yO_2$ (y = 0.005, 0.01, 0.025, 0.05 and 0.1) calcined at 750°C for 30 h

Table 1: Data calculated from XRD patterns of $LiNi_{1-y}Tl_yO_2$ (y = 0.005, 0.01, 0.025, 0.05 and 0.1) calcined at 750°C for 30 h

	a(Å)	c(Å)	I_{003}/I_{104}	R-factor	Unit cell volume (Å^3)
y = 0.1	2.786	14.178	1.02	0.59	101.872
y = 0.05	2.880	14.223	1.12	0.53	101.320
y = 0.025	2.877	14.195	1.05	0.56	102.240
y = 0.01	2.877	14.207	0.98	0.52	101.843
y = 0.005	2.882	14.239	1.16	0.50	102.108



(a) y = 0.1 (b) y = 0.05

(c) y = 0.025 (d) y = 0.01

(e) y=0.005

Fig. 3: SEM photographs of $LiNi_{1-y}Tl_yO_2$ (y = 0.005, 0.01, 0.025, 0.05 and 0.1) calcined at 750°C for 30 h

Figure 3 shows the SEM photographs of $LiNi_{1-y}Tl_yO_2$ (y = 0.005, 0.01, 0.025, 0.05 and 0.01) calcined at 750°C for 30 h. The samples contain small and large particles. The particles become larger as the value of y increases.

Figure 4 shows the variations of the discharge capacity of $LiNi_{1-y}Tl_yO_2$ (y = 0.005, 0.01, 0.025, 0.05 and 0.01) calcined at 750°C for 30 h. The sample with y = 0.05 has the largest first discharge capacity 179.8 mAh g^{-1} and the discharge capacity 113.8 mAh g^{-1} at the 20th cycle. The sample with y = 0.005 has the smallest first discharge capacity 125.4 mAh g^{-1}. The samples exhibit similar cycling performance.

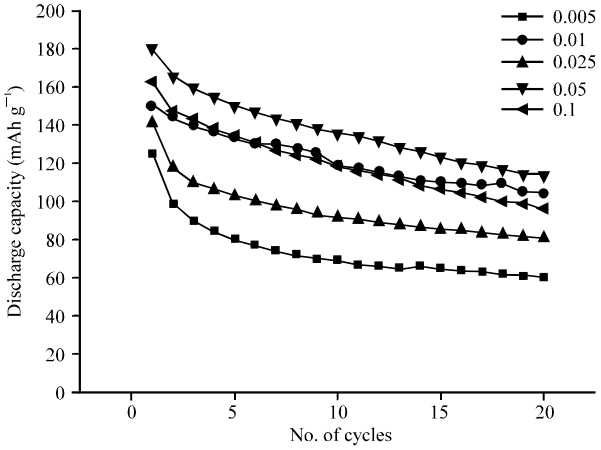


Fig. 4: Variations of discharge capacity at 0.1C-rate with the number of cycles for $LiNi_{1-y}Tl_yO_2$ (y = 0.005, 0.01, 0.025, 0.05 and 0.1) calcined at 750°C for 30 h

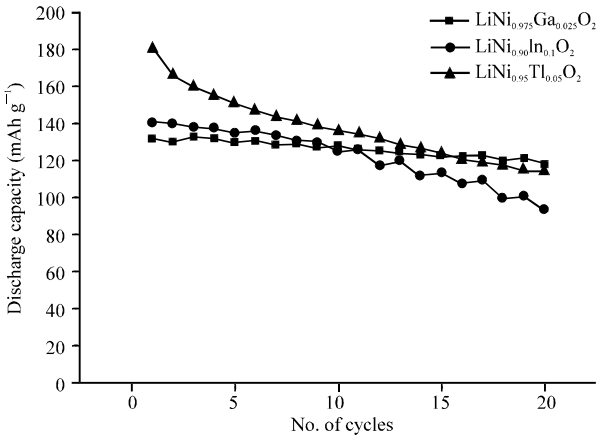


Fig. 5: Variations of discharge capacity at 0.1 C-rate with the number of cycles for $LiNi_{1-y}M_yO_2$ (M = Ga, y = 0.025; M = In, y = 0.1; M = Tl, y = 0.05) calcined at 750°C for 30 h

Table 2: Data calculated from X-ray powder diffraction patterns of $LiNi_{1-y}M_yO_2$ (M = Ga, y = 0.025; M = In, y = 0.1; M = Tl, y = 0.05) calcined at 750°C for 30 h

	a(Å)	c(Å)	I_{003}/I_{104}	R-factor	Unit cell volume (Å^3)
$LiNi_{0.975}Ga_{0.025}O_2$	2.883	14.362	0.92	0.54	103.380
$LiNi_{0.90}In_{0.1}O_2$	2.877	14.212	1.33	0.52	101.559
$LiNi_{0.95}Tl_{0.05}O_2$	2.880	14.223	1.12	0.53	101.320

In our earlier study (Kim *et al*., 2005a, b), we studied the electrochemical properties of $LiNi_{1-y}Ga_yO_2$ and $LiNi_{1-y}In_yO_2$ synthesized by the same method, as mentioned above. Among $LiNi_{1-y}Ga_yO_2$ $LiNI_{0.975}Ga_{0.025}O_2$ had the best electrochemical properties. $LiNi_{0.9}In_{0.1}O_2$ exhibited the best electrochemical properties among $LiNi_{1-y}In_yO_2$.

Figure 5 shows the variations of the discharge capacity of $LiNi_{1-y}M_yO_2$ (M = Ga, y = 0.025; M = In, y = 0.1; M = Tl, y = 0.05) calcined at 750° for 30 h. The sample $LiNi_{0.95}Tl_{0.05}O_2$ has the largest first discharge capacity 179.8 mAh g^{-1} and the discharge capacity 113.8 mAh g^{-1} at the 20th

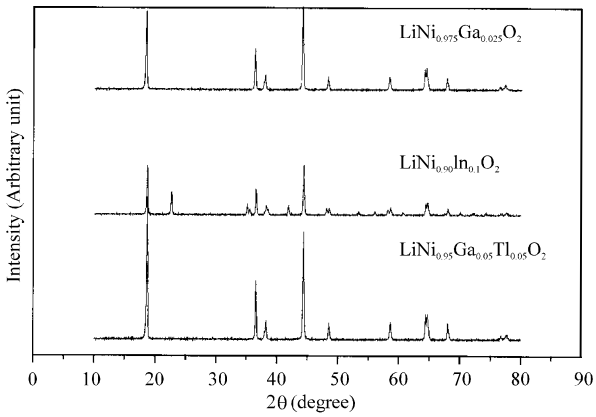
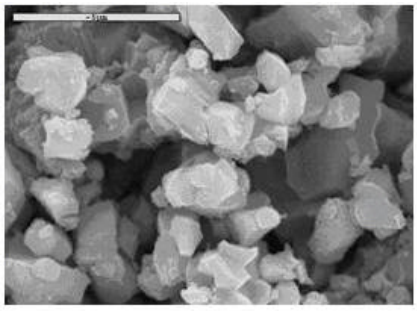
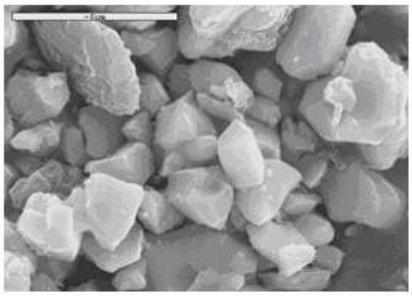


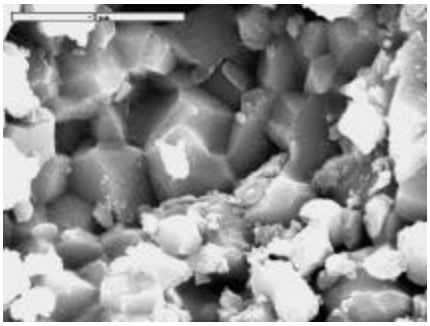
Fig. 6: X-ray powder diffraction patterns of $LiNi_{1-y}M_yO_2$ (M = Ga, y = 0.025; M = In, y = 0.1; M = Tl, y = 0.05) calcined at 750°C for 30 h



(a) $LINi_{0.975}Ga_{0.025}O_2$



(b) $LiNi_{0.90}In_{0.1}O_2$



(c) $LiNi_{0.95}Tl_{0.05}O_2$

Fig. 7: SEM photographs of $LiNi_{1-y}M_yO_2$ (M = Ga, y = 0.025; M = In, y = 0.1; M = Tl, y = 0.05) calcined at 750°C for 30 h

cycle. The sample $LiNi_{0.975}Ga_{0.025}O_2$ has the smallest first discharge capacity 131.4 mAh g^{-1}, but it has the best cycling performance. $LiNi_{0.975}Ga_{0.025}O_2$ has the discharge capacity 117.5 mAh g^{-1} at the 20th cycle, showing the discharge capacity degradation rate of 0.70 mAh g^{-1} $cycle^{-1}$.

Figure 6 shows XRD *patterns* of $LiNi_{0.975}Ga_{0.025}O_2$, $LiNi_{0.9}In_{0.1}O_2$ and $LiNi_{0.95}Tl_{0.05}O_2$. All the samples have the phase with $R\bar{3}m$ structure. In addition, $LiNi_{0.9}In_{0.1}O_2$ shows the peaks for $LiInO_2$.

Table 2 gives the lattice parameters a, c, c/a, I_{003}/I_{104}, R-factor and unit cell volume calculated from XRD patterns of $LiNi_{1-y}M_yO_2$ (M = Ga, y = 0.025; M = In, y = 0.1; M = Tl, y = 0.05). $LiNi_{0.9}In_{0.1}O_2$ has the largest I_{003}/I_{104} and all the samples have the similar values of R-factor.

Figure 7 shows the SEM photographs of $LiNi_{0.975}Ga_{0.025}O_2$, $LiNi_{0.9}In_{0.1}O_2$ and $LiNi_{0.95}Tl_{0.05}O_2$ calcined at 750°C for 30 h. All the samples have small and large particle. The particle size increases roughly from $LiNI_{0.975}Ga_{0.025}O_2$ to $LiNi_{0.9}In_{0.1}O_2$ and then to $LiNi_{0.95}Tl_{0.05}O_2$. The particles of $LiNi_{0.95}Tl_{0.05}O_2$ are agglomerated.

Conclusions

$LiNi_{1-y}Tl_yO_2$ (y = 0.005, 0.01, 0.025, 0.05 and 0.1) were synthesized by milling for 1 h, preheating at 450°C for 5 h in air, then pelletizing and finally calcining at 750°C for 30 h under oxygen stream. All the samples had the $R\bar{3}m$ structure. $LiNi_{0.95}Tl_{0.05}O_2$ has the largest first discharge capacity 179.8 mAh g^{-1} and the discharge capacity 113.8 mAh g^{-1} at the 20th cycle. $LiNi_{0.995}Tl_{0.005}O_2$ has the smallest first discharge capacity 125.4 mAh g^{-1}. The samples exhibit similar cycling performances. $LiNi_{0.975}Ga_{0.025}O_2$ and $LiNi_{0.9}In_{0.1}O_2$ had the best electrochemical properties among the samples substituted by the same element, respectively. Among $LiNi_{0.975}Ga_{0.025}O_2$, $LiNi_{0.9}In_{0.1}O_2$ and $LiNi_{0.95}Tl_{0.05}O_2$, $LiNi_{0.95}Tl_{0.05}O_2$ has the largest first discharge capacity, but has the worst cycling performance. $LiNi_{0.975}Ga_{0.025}O_2$ has the smallest discharge capacity, but has the smallest capacity degradation rate 0.70 mAh g^{-1} $cycle^{-1}$.

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