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Supporting Information

Revealing the chemistry of an anode-passivating electrolyte salt for high rate and stable sodium metal batteries

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Experimental section

Storage testing. The storage tests of the electrolytes and sodium were performed as follows. A Na metal disk (0.95 cm^2) was soaked in 1.0 M NaDFOB in EC:DMC, in 1.0 M $NaPF_6$ in EC:DMC, and in EC:DMC solutions, respectively, which were stored in a glove box at room temperature. The solutions were periodically taken for ^{1}H and ^{13}C NMR analysis.

Quantitative NMR measurements. Separators collected from the cells after 1st, 10th, 20th, 50th and 100th cycling were immersed in 5 g acetonitrile. Then the collected separators were centrifuged at the rate of 2000 revs/min for 5 min to fully extract electrolyte from the separators. 100 μL supernatant were taken for ^{1}H NMR analysis with 100 μL diluted benzene added as an internal standard. The amount of solvent was quantified by the integration relative to the ^{1}H signal of the internal standard. The signal of separators obtained from the cells containing stainless-steel electrodes without cycling was defined as 100%.

Electrode analysis. After electrochemical tests, the symmetric cells were carefully disassembled in a glove box filled with argon to obtain sodium electrodes for SEM, solid-state NMR, and XPS analysis. The sodium electrodes were washed with dimethyl carbonate (DMC) several times to remove residual electrolyte and fully dried in the glove box. During transfer, the sodium electrodes were protected with Ar in homemade container to avoid contacting with the air. The SEI products were collected by carefully scraping them with a sharp surgical blade from the sodium surface for solid-state NMR measurements.

Solid-state NMR spectroscopy. Magic angle spinning (MAS) experiments were conducted using 3.2 mm triple-resonance probes at a spinning rate of 10 kHz or 15 kHz. The spectra were collected at Larmor frequencies of 158.7 MHz for ^{23}Na, 192.4 MHz for ^{11}B, 376.4 MHz for ^{19}F, and 242.8 MHz for ^{31}P. The ^{23}Na spectra are referenced to 1 M NaCl solution at 0 ppm, ^{11}B spectra are referenced to 0.1 M H_3BO_3 solution at 19.3 ppm, ^{19}F spectra are referenced to CF_3COONH_4 at -72 ppm, and ^{31}P spectra are referenced to ammonium dihydrogen phosphate at 0.81 ppm. 1D ^{23}Na spectra were collected via direct excitation at the radio frequency (RF) field of 147 kHz, with a relaxation delay time of 2 s. Solid echo pulse sequence was used to acquire 1D ^{11}B spectra. The multiple quantum magic angle spinning (MQMAS) pulse sequence used for the ^{23}Na and ^{11}B experiments was the four-pulse version with a z-filter.

Figures

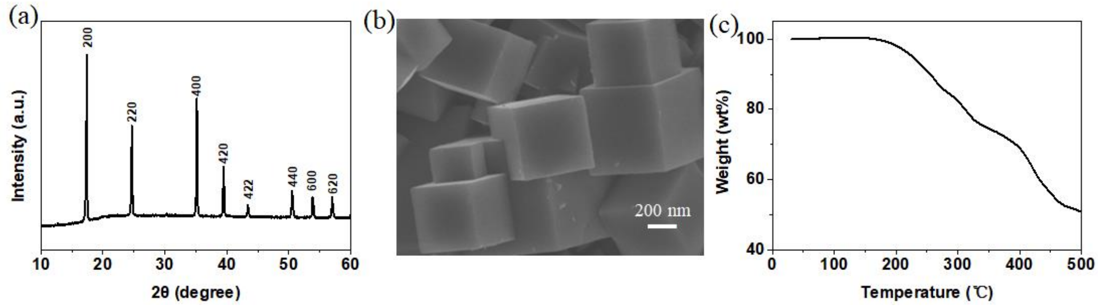

Fig. S1 Characterization of Prussian blue (PB) material. (a) X-ray diffraction pattern, (b) SEM image and (c) TG curves of PB material.

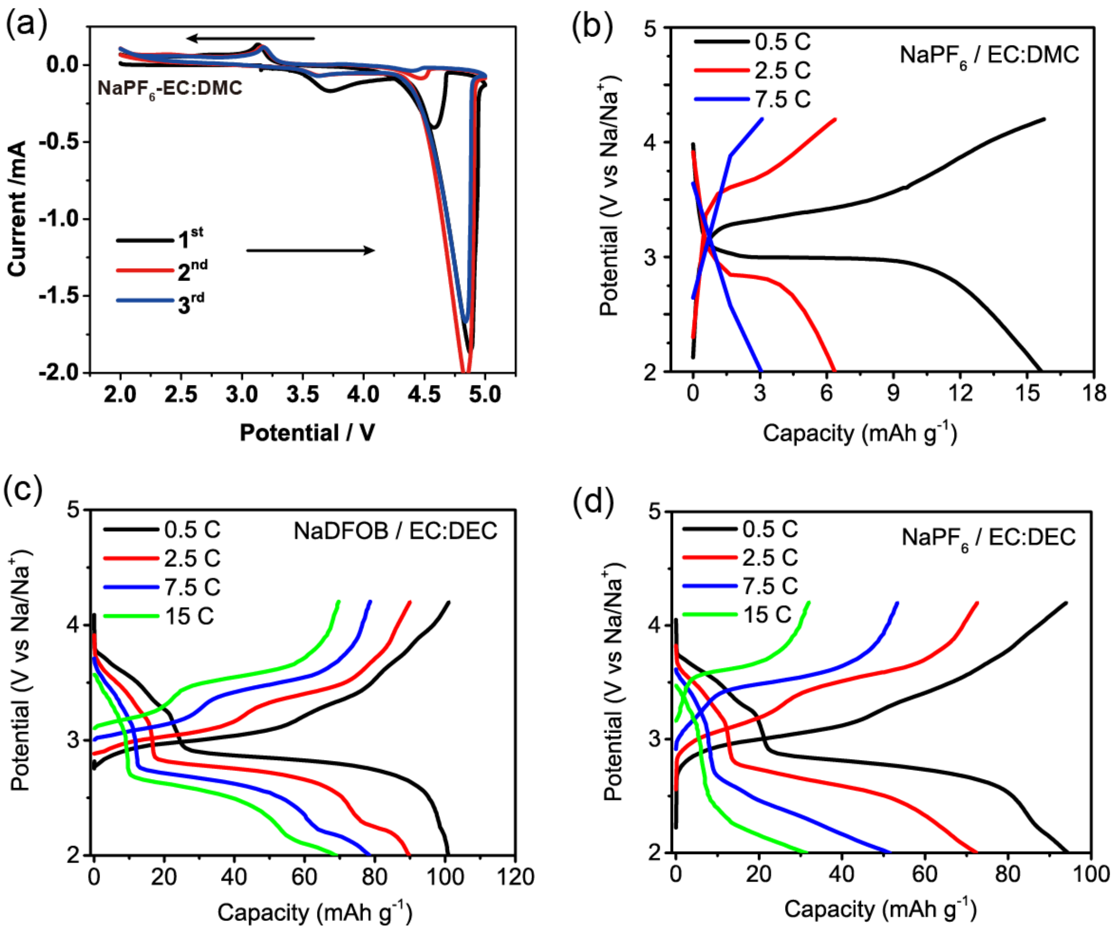

Fig. S2 Electrochemical performance of PB/Na cells. (a) Cyclic voltammograms of the PB/Na cells using the $NaPF_6$-EC:DMC electrolyte for the initial three cycles. Charge/discharge profiles at different rates for PB/Na cells with the electrolyte (b) $NaPF_6$-EC:DMC, (c) NaDFOB-EC:DEC, and (d) $NaPF_6$-EC:DEC.

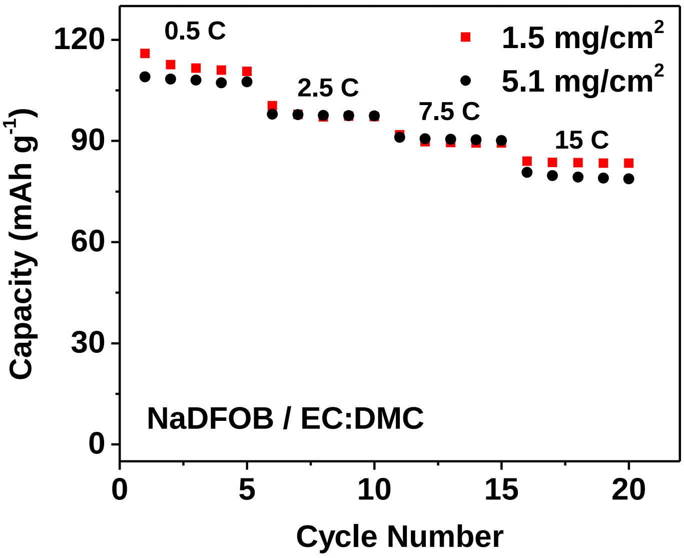

Fig. S3. Rate capability for PB/Na cells using NaDFOB-EC:DMC electrolyte with different loading of cathode.

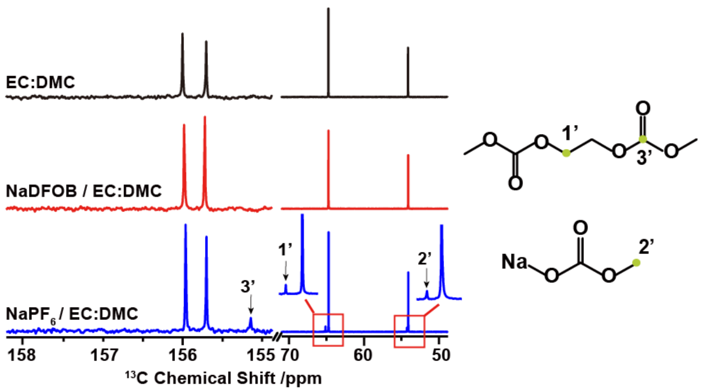

Fig. S4 ^{13}C NMR spectra of solutions soaked with Na metal. Black: EC:DMC, red: 1.0 M NaDFOB in EC:DMC, blue: 1.0 M $NaPF_6$ in EC:DMC.

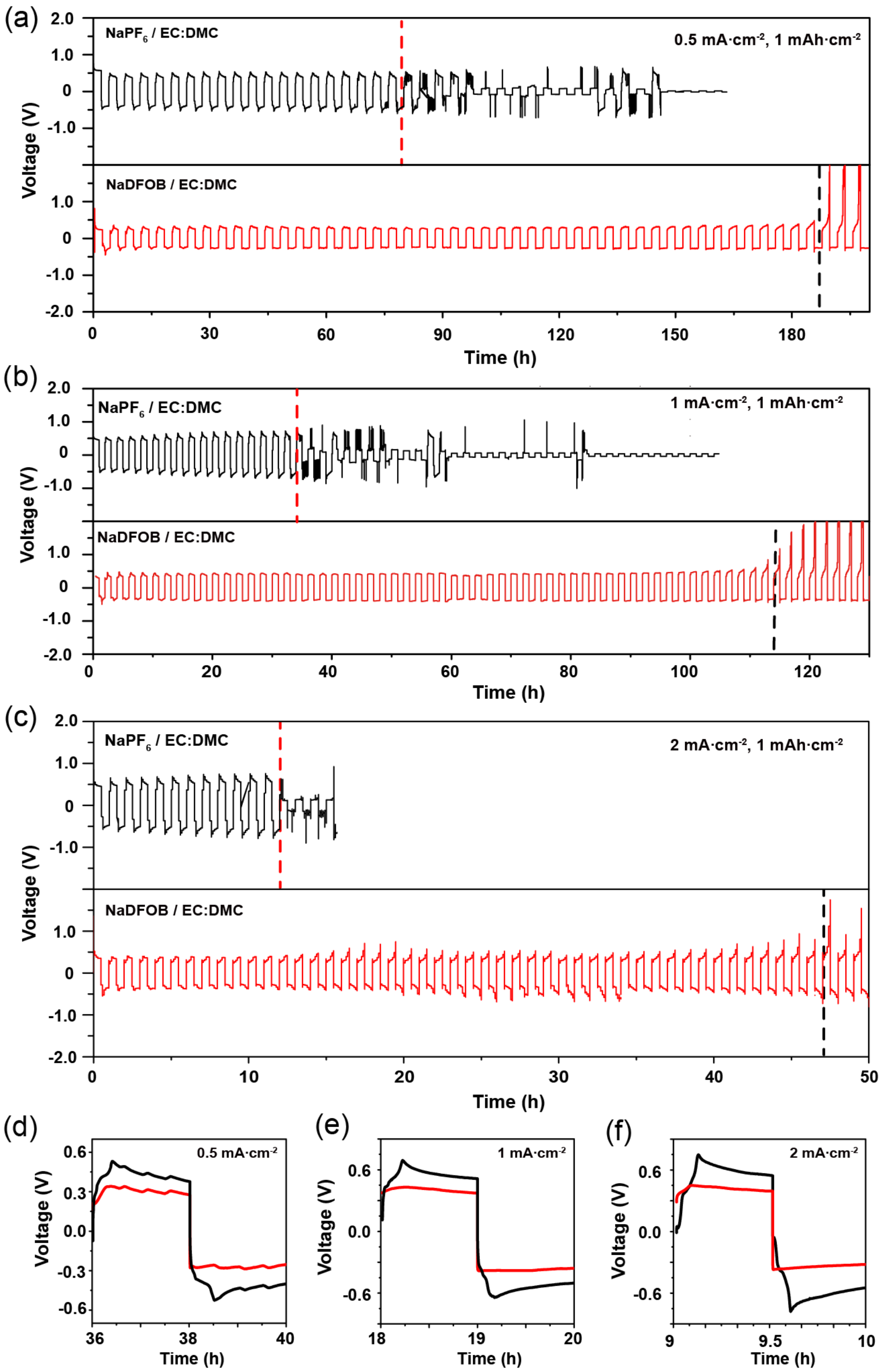

Fig. S5 Voltage profiles of symmetric cells. The cells were evaluated with electrolytes consisting of 1.0 M NaDFOB (red) and 1.0 M $NaPF_6$ (black) in EC:DMC. Galvanostatic cycling performance of the cells at different current densities: (a) 0.5 $mA\cdot cm^{-2}$, (b) 1 $mA\cdot cm^{-2}$, and (c) 2 $mA\cdot cm^{-2}$ with a capacity of 1 $mAh\cdot cm^{-2}$. (d-f) Zoomed-in views of the voltage profiles of NaDFOB-based cells (red) and $NaPF_6$-based cells (black) at the 10^{th} cycle.

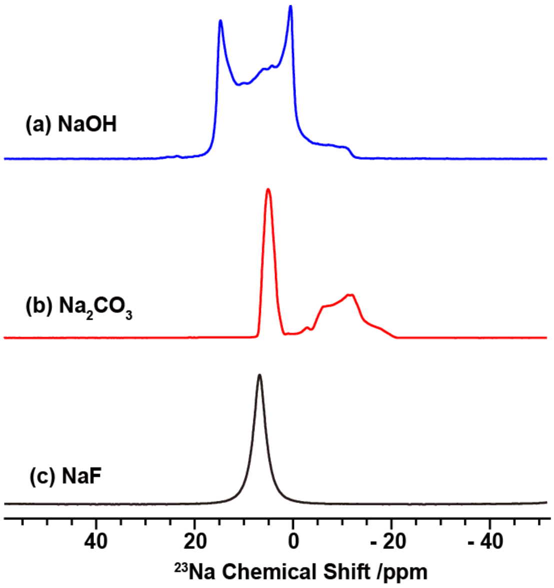

Fig. S6 1D ^{23}Na onepulse MAS NMR spectra of reference samples. (a) Sodium hydroxide, (b) sodium carbonate, and (c) sodium fluoride.

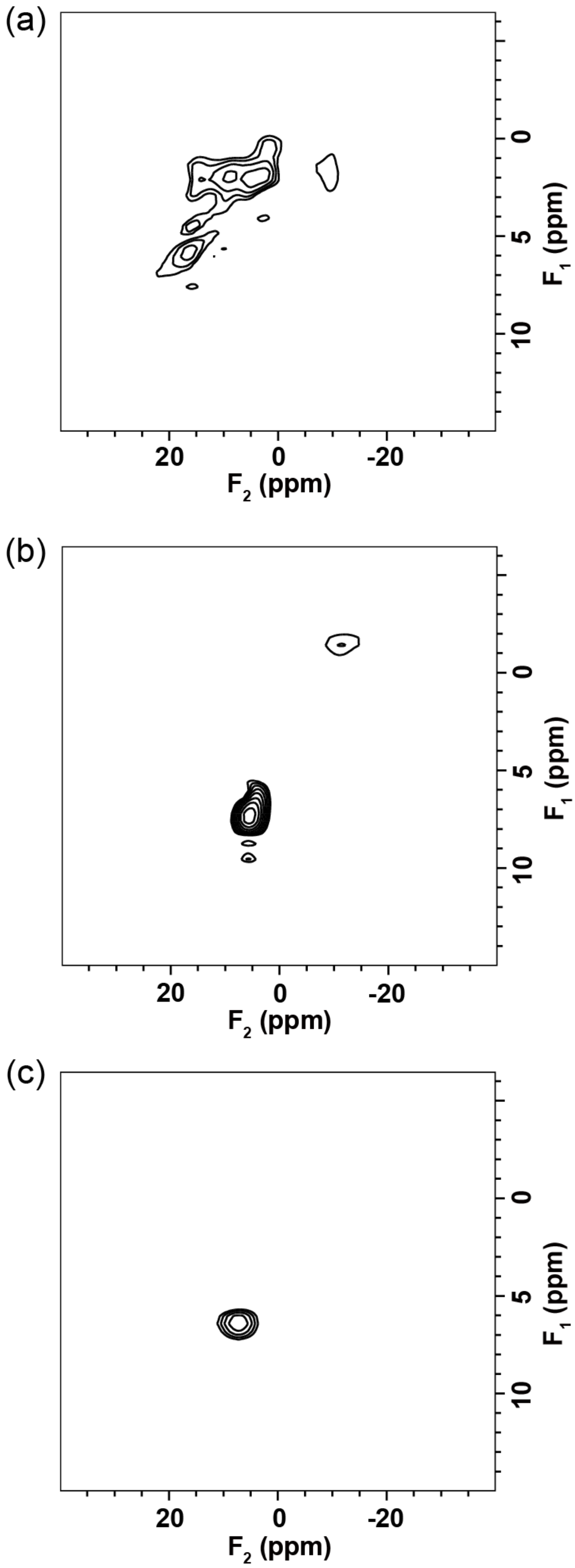

Fig. S7 2D ^{23}Na-3QMAS NMR spectra of reference samples. (a) Sodium hydroxide, (b) sodium carbonate, and (c) sodium fluoride.

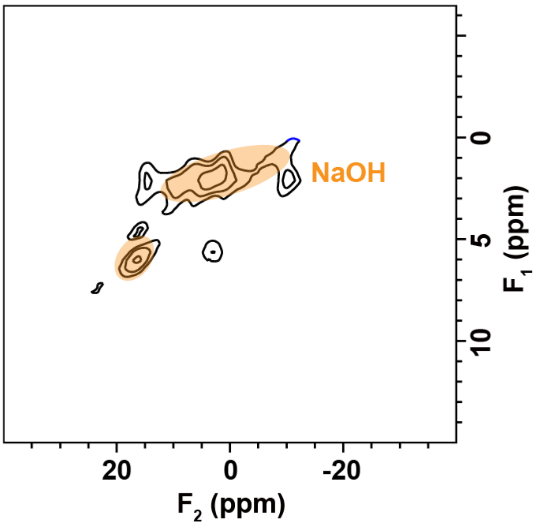

Fig. S8 2D ^{23}Na-3QMAS NMR spectrum of SEI in $NaPF_6$-based cells.

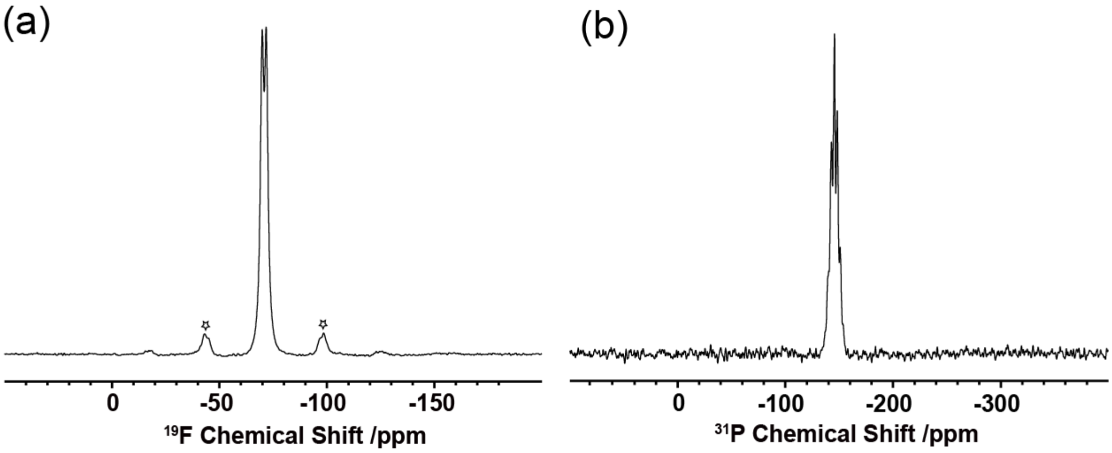

Fig. S9 NMR spectra of SEI in $NaPF_6$-based cells. (a) ^{19}F spectrum. The asterisks denote the spinning sidebands (spinning rate of 10 kHz). (b) ^{31}P spectrum.

Tables

Table S1. Element contents of PB.

	Na	Fe	C	N
PB	4.6% ± 0.2	33.1% ± 0.1	21.9% ± 0.1	24.8% ± 0.1

Table S2. The simulated ^{23}Na quadrupolar parameters for species in NaDFOB-based SEI.

Compound		δ_{iso} (ppm)	C_Q (MHz)	η
Na_2CO_3-Na1	Lit.[1]	7.5	1.28	0.50
	Exp.	7.5	1.28	0.50
Na_2CO_3-Na2	Lit.[1]	-4	2.48	0.65
	Exp.	2.8	2.61	0.42
$Na_4B_2O_5$-Na1	Lit.[2]	19.6	2.2	1.0
	Exp.	17.3	2.19	1.00
$Na_4B_2O_5$-Na2	Lit.[2]	14.4	3.0	0.5
	Exp.	12.5	2.87	0.45
NaF	Lit.[1]	7.4	0	0
	Exp.	7.4	0	0
NaOH	Lit.[1]	20.5	3.6	0.15
	Exp.	25.5	3.05	0.15
NaDFOB	Exp.	-13.7	1.52	0.97
$NaBF_4$	Lit.[3]	-	1.01	0.1
	Exp.	-18.5	1.04	0.53

Table S3 The simulated ^{11}B quadrupolar parameters for species in NaDFOB-based SEI.

Compound		δ_{iso} (ppm)	C_Q (MHz)	η
$NaBF_4$	Lit.[3]	-	0.06	0.65
	Exp.	-1.9	0.06	0.65
NaDFOB	Exp.	2.7	0.14	0.01
$Na_4B_2O_5$	Lit.[4]	21.9 ± 0.2	2.63 ± 0.02	0.50 ± 0.04
	Exp.	21.4	2.65	0.55

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