Supporting Information

Na[Mn$_{0.36}$Ni$_{0.44}$Ti$_{0.15}$Fe$_{0.05}$]O$_2$ predicted via machine learning for high energy Na-ion batteries

Saaya Sekine,[1] Tomooki Hosaka,[1] Hayato Maejima,[1] Ryoichi Tatara,[1] Masanobu Nakayama,[2] and Shinichi Komaba[1]

1: Department of Applied Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, Japan

2: Nagoya Institute of Technology., Gokisho, Showa, Nagoya, 466-8555

Experimental

Machine learning model construction:

A database of 95 O3-type $NaMeO_2$ compositions and 107 charge-discharge data of Na half cells evaluated in our group was used as training and test data for machine learning. The larger number of charge-discharge data is because some materials are tested in the different voltage range. The database includes the composition of $NaMeO_2$ (Me = Mn, Ni, Ti, Zn, Fe, Sn, Co, Mg, Cu, Al, W), upper and lower voltage limits of charge-discharge tests, initial discharge capacity, average discharge voltage, and capacity retention after 20 cycles. The compositions and upper and lower voltage limits were utilized as explanatory variables to predict the initial discharge capacity, the average initial discharge voltage, and the capacity retention after 20 cycles. The charge-discharge tests were conducted with R2032-type coin cells assembled in an Ar-filled glove box. The separator was a glass filter (Advantec), and the counter electrode was Na metal (purity >99%, Kanto Chemical Co, Ltd.).

The regression was performed with Random Forest and LightGBM algorithm from the Scikit-learn (1.0.2) library in Python (3.9.12). The training data was 80% of the total data, and 10 cross-validation was used for training. Hyperparameter tuning of these models was conducted by grid search. The rest 20% of the data was used as test data to verify the accuracy of the predictions using root mean squared error (RMSE). Finally, the RMSE of Random Forest and LightGBM were compared, and the best model was selected. The hyperparameters in the LightGBM model for predicting initial discharge capacity were minimum data in leaf = 5, leaf number = 8, and verbose = −1. The parameters of Random Forest model for predicting average discharge voltage are depth of decision tree = 10, leaf number = 1, and number of decision tree = 500. The parameters of Random Forest model for predicting 20th capacity retention are depth of decision tree = 4, leaf number = 1, and number of decision tree = 100. The impacts of explanatory variables on the objective variable were analyzed with Shap.

Promising composition search

The constructed model was used to search for promising compositions. In order to conduct an efficient search, multi-objective Bayesian optimization with Optuna was employed. The objective variables were energy density and capacity retention at the 20th cycle, and optimization was performed to maximize the two parameters. The upper and lower voltage limits was fixed to 2.0 and 4.2 V, respectively. The compositional range for optimization was limited in a quaternary phase diagram end members of $NaMnO_2$, $NaMnNiO_2$, $NaFeO_2$, $NaNiTiO_2$.

Synthetic procedures

$NaMn_{0.36}Ni_{0.44}Ti_{0.15}Fe_{0.05}O_2$ prepared by a solid-state reaction. A reagent grade Na_2CO_3 (Nacalai Tesque, Inc., 99.8%), and $Ni(OH)_2$ (Wako Co., Inc., > 95.0%), and Mn_2O_3 prepared by calcining $MnCO_3$ (Kishida Chem. Co., Ltd., 44% as Mn content) at 700 °C were mixed at stoichiometric ratio by planetary ball-milling with acetone at 600 rpm for 12 h by using a planetary ball mill (PULVERISETTE 7 classic line, FRITSCH GmbH). The mixture was dried and pressed into pellets,

followed by heating for 24 h in air at 800 °C. After the calcination, the samples were taken out from the furnace without cooling process, and then immediately transferred into an argon-filled glove box. The samples were cooled to room temperature in the glove box and were kept inside to avoid the exposure to moisture in air.

Structural characterization

The structure of NaMnNiTiFeO$_2$ synthesized using a laboratory-scale X-ray diffractometer (MultiFlex, Rigaku Corporation: operated at 40 kV / 30 mA) equipped with a Cu Kα X-ray source and Ni filter was investigated by X-ray diffraction (XRD). To avoid exposure of the sample to air, a homemade sealed sample holder was used for the measurements. After the electrochemical test, the composite electrode was removed from the coin cell, washed with diethyl carbonate (DEC, Kishida Chemical) to remove electrolyte salts, and dried in an Ar-filled glove box before measurement. To minimize the effect of X-ray absorption by the sample, the wavelength of the incident X-ray was set to 0.8 Å using a silicon monochromator, and calibration was performed using the NIST reference material 640d SiO$_2$ as the external standard material.[1]

Surface and morphological characterization

Particle morphology was observed using scanning electron microscopy (SEM). A scanning electron microscope (JCM-6000, JEOL Ltd.) operating at an acceleration voltage of 15 kV was used to observe SEM images.

Electrochemical characterization

☐For the electrochemical tests, R2032-type coin cells assembled in an Ar-filled glove box were used. The electrolyte was 1 mol dm^{-3} NaPF$_6$ in PC:EC =1:1 (v/v) (Kishida Chemical Co, Ltd.), the separator was a glass filter (Advantec), and the counter electrode and reference electrode were Na metal (purity >99%, Kanto Chemical Co, Ltd.) The sodium half-cell was assembled.

The composite electrode was made by mixing 80 wt.% active material, 10 wt.% acetylene black (AB, Strem Chemicals, Inc.) as a conductivity aid, and 10 wt.% polyvinylidene fluoride (PVdF, Polysciences, Inc.) as a binder, and dispersing them in an appropriate amount of N-methylpyrrolidone (NMP, Kanto Chemical Co., Ltd.). The slurry was applied to Al foil and dried at 100°C under vacuum. The electrode sheet was punched into a disk shape to make the working electrode. The mass of active material per unit area was 1-3 mg cm^{-2}.

Constant-current charge/discharge tests were conducted at 25°C mainly at a current rate of C/20 (12.7 mA g^{-1}) using a charge/discharge measuring device (TOSCAT-3100, TOYO System Co., Ltd.). The voltage ranges were 2.0 V -4.2 V and 2.0-4.1 V.
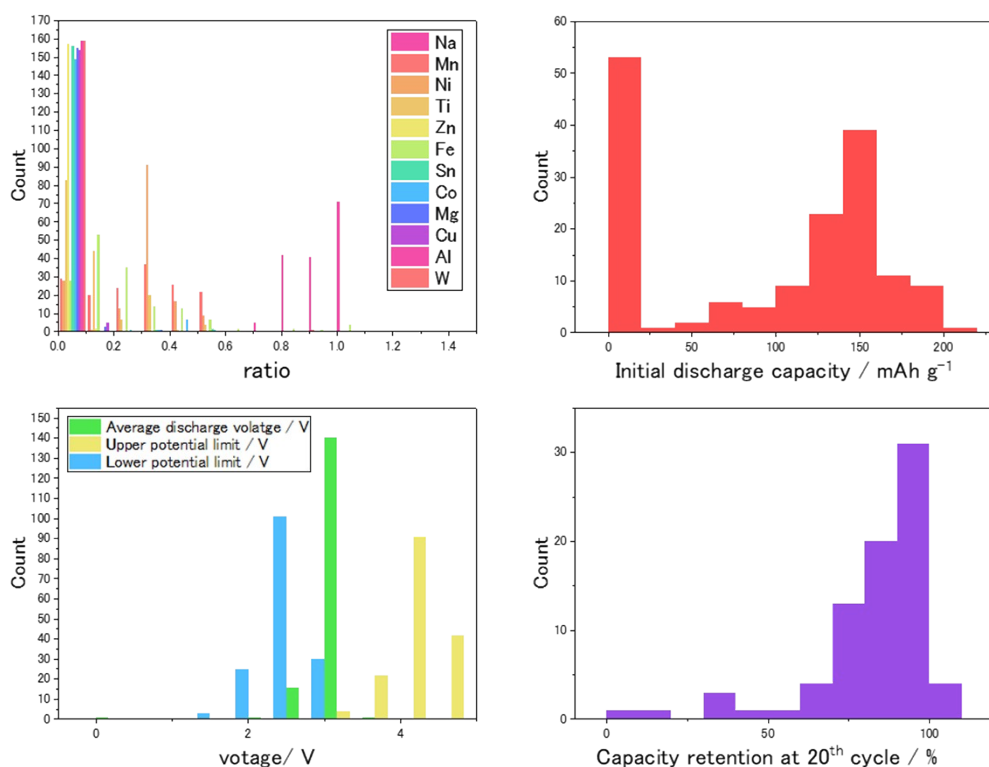
Figure S1 Histogram of the dataset used in this study

Table S1 The Root Mean Square Error (RMSE) for each of the eight models used was calculated for each of the objective variables.

	Initial discharge capacity		Mean discharge voltage		Capacity retention at 20th	
	Train RMSE (mAh/g)	Test RMSE (mAh/g)	Train RMSE (V)	Test RMSE (V)	Train RMSE (%)	Test RMSE (%)
Elastic net	**24.17**	**28.64**	**0.147**	**0.113**	**8.566**	**7.002**
Kernel SVR	**21.03**	**27.92**	**0.137**	**0.102**	**7.737**	**6.685**
Lasso	**24.17**	**28.64**	**0.160**	**0.119**	**8.545**	**7.002**

LightGBM	22.02	15.81	0.109	0.0641	7.455	4.735
Linear SVR	24.66	28.37	0.157	0.115	8.318	8.954
PLS	24.81	17.56	0.153	0.112	8.730	5.529
Random forest	24.61	25.06	0.102	0.0565	7.448	4.560
Ridge	24.96	28.92	0.150	0.115	9.091	6.924
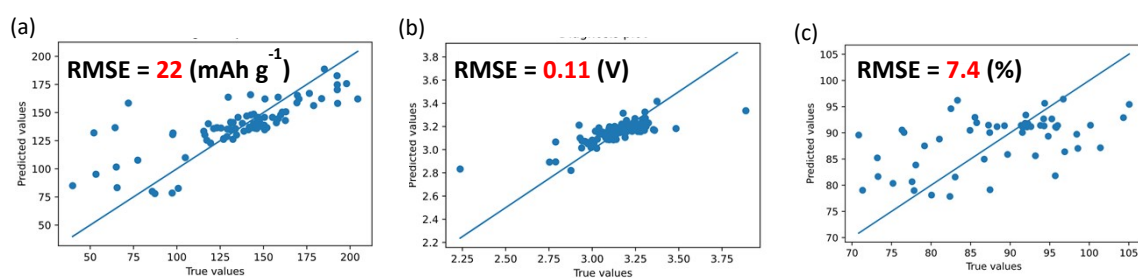
Figure S2□ Train data results of (a) initial discharge capacity (LightGBM) (b) average discharge voltage(Random Forest) (c) capacity retention at 20th cycle (Random Forest) and test data results. LightGBM is employed for the discharge capacity and Random Forest was employed for discharge voltage and capacity retention.

Table S2 Compare RMSE calculated excluding records with overlapping compositions and records with overlapping both composition and charge/discharge voltage.

	Excluded duplicate compositions	Excluded duplicate composition & condition	Include duplicate composition
Initial discharge capacity (mAh/g)	14.59	15.92	15.81
discharge voltage (V)	0.05686	0.05834	0.05652
Capacity retention at 20th (%)	4.685	6.509	4.560
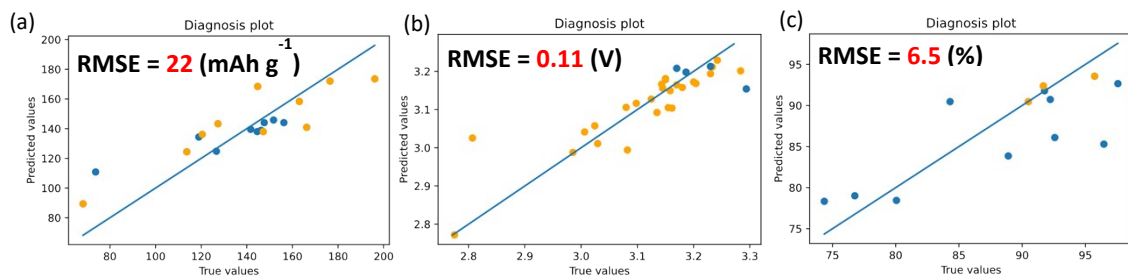
Figure S3□ Figure 2 with records with overlapping compositions shown in orange.

Contribution to expected average discharge voltage
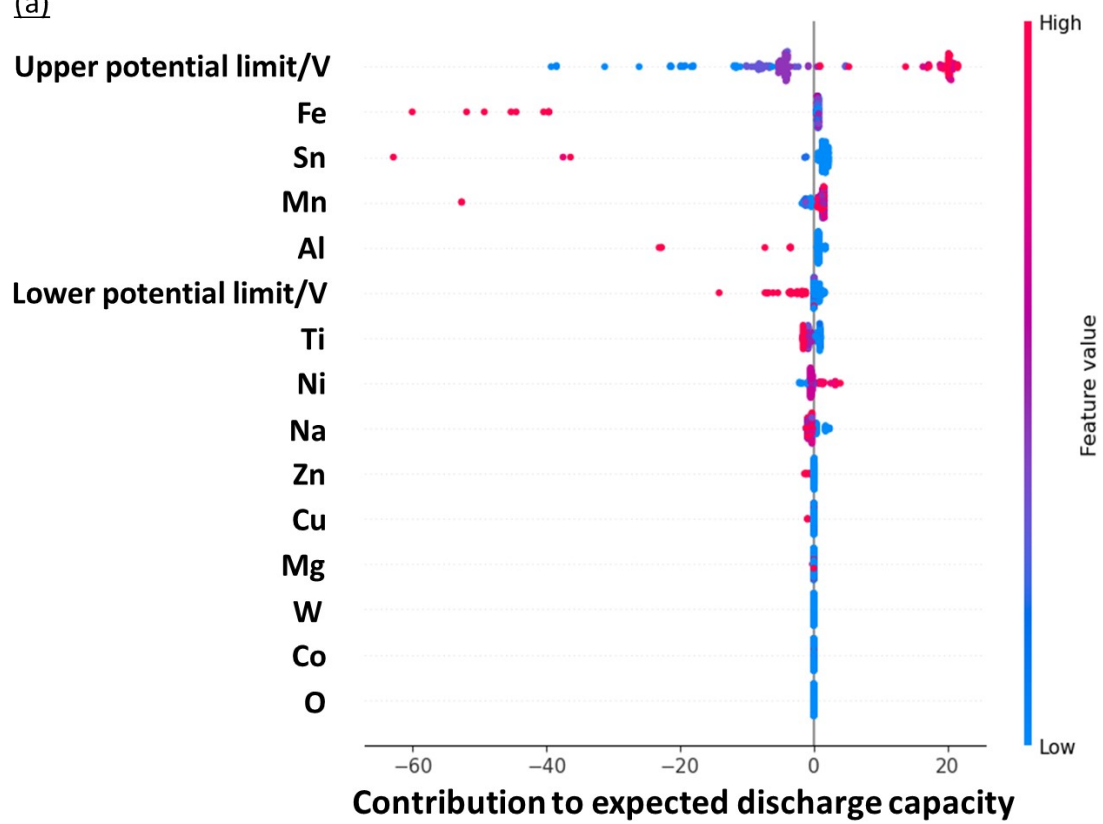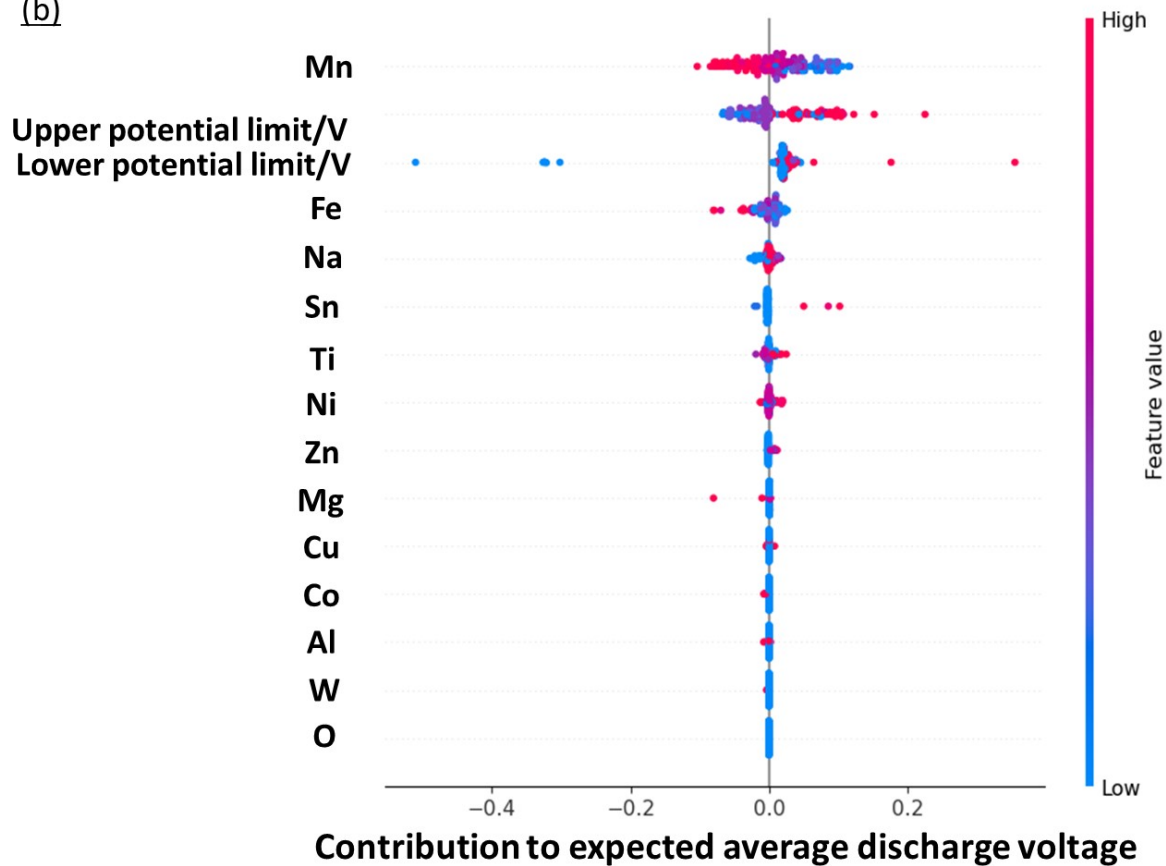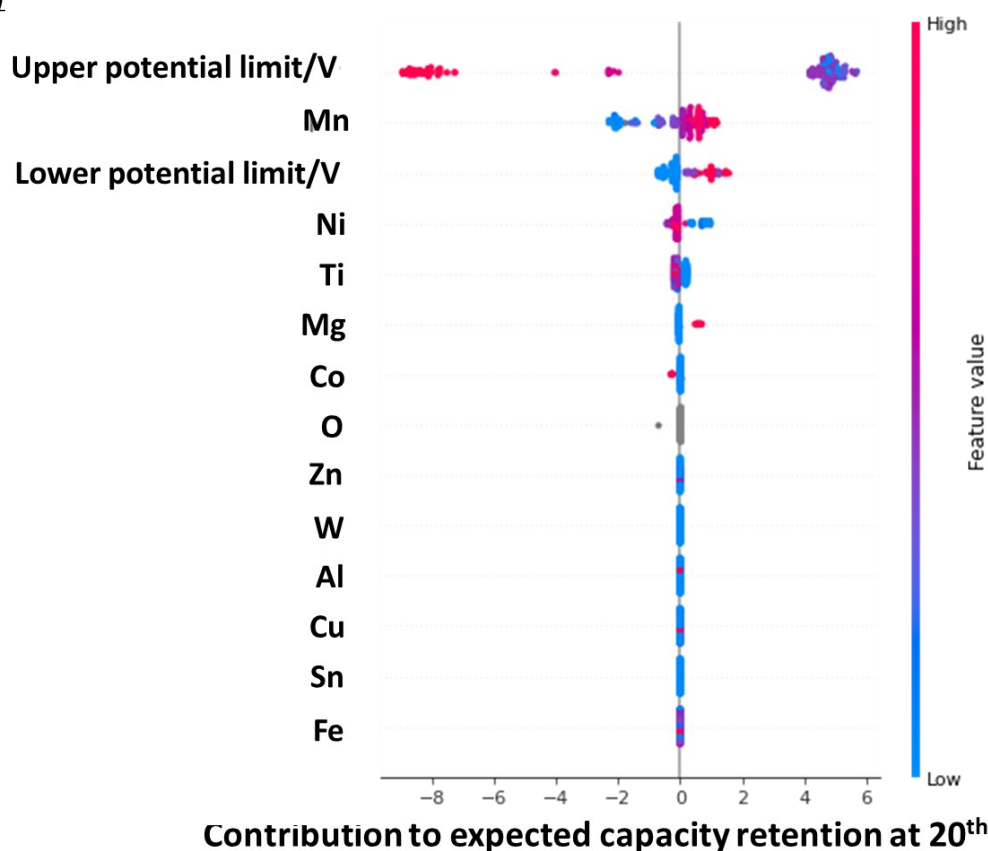
(c)

Figure S4 For a model that predicts (a)initial discharge capacity (b)average discharge voltage, (c)capacity retention at 20th cycle the magnitude of the impact of each descriptor on the objective value.

Table S3 Each parameter by Rietveld refinement.

Space group *R*-3*m*						
a = 2.96651(5) Å, c = 16.02401(18) Å, V = 122.1215(33)×10⁻³⁰ m³						
Atom	x	y	z	g	B / Å²	Wyckoff position
Na	0	0	0.5	1.0000	1.000	3b
Mn	0	0	0	0.3730	0.400	3a
O	0	0	0.2678	1.0000	0.900	6c

Ni	0	0	0	0.4290	0.400	3a
Fe	0	0	0	0.0440	0.400	3a
Ti	0	0	0	0.1520	0.400	3a

TableS4 The result of ICP measurement.

	Na	Mn	Ni	Ti	Fe
Target	1	0.341	0.449	0.164	0.045
Results	1.06	0.373	0.429	0.152	0.044

The measured weight % value was divided by the atomic weight and corrected so that the value totaled 1 for the transition metals to give the calculated result.
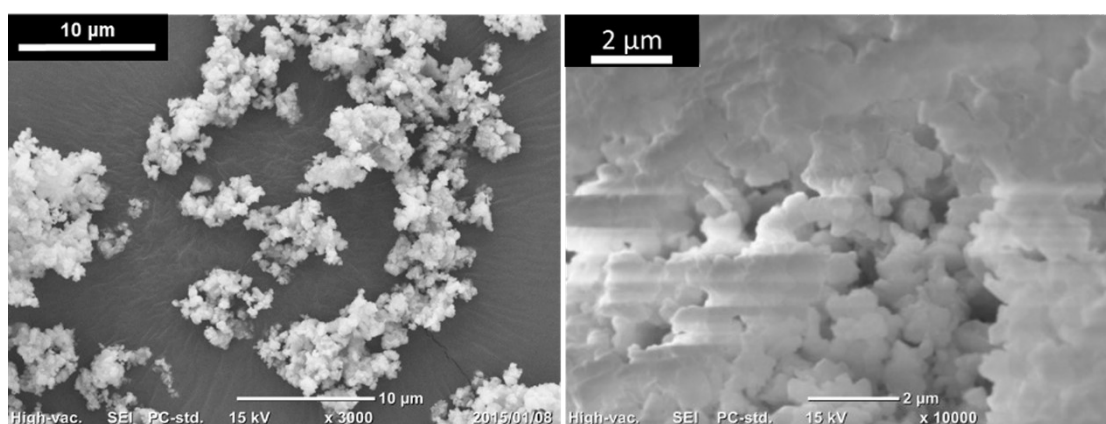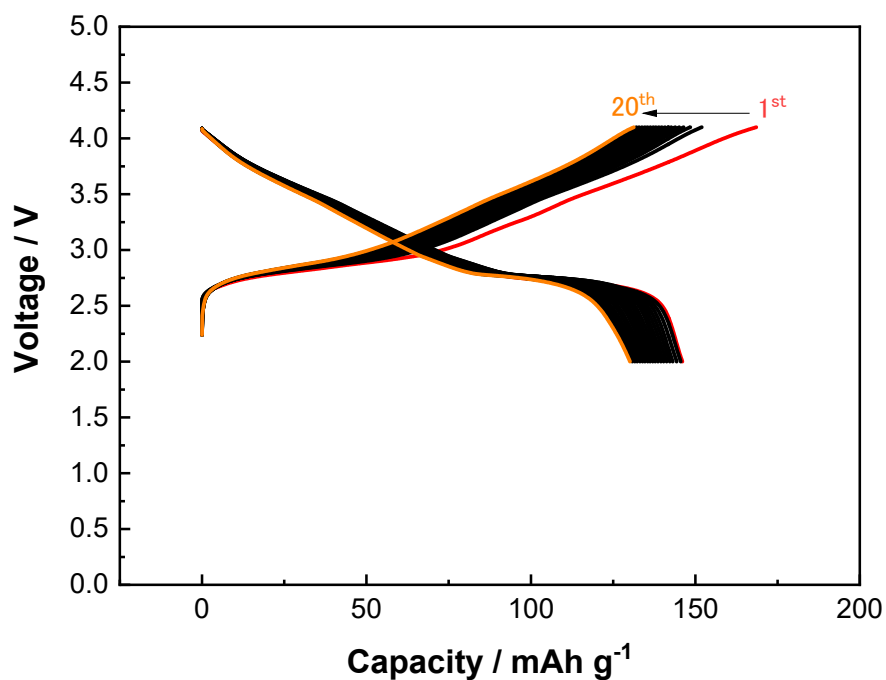

FigureS5 The image of SEM of MNTF

Figure S6 Results of charge/discharge tests in the voltage range of 2.0 V-4.1 V for MNTF.

Table S5 Comparison of predicted and measured MNTF values.

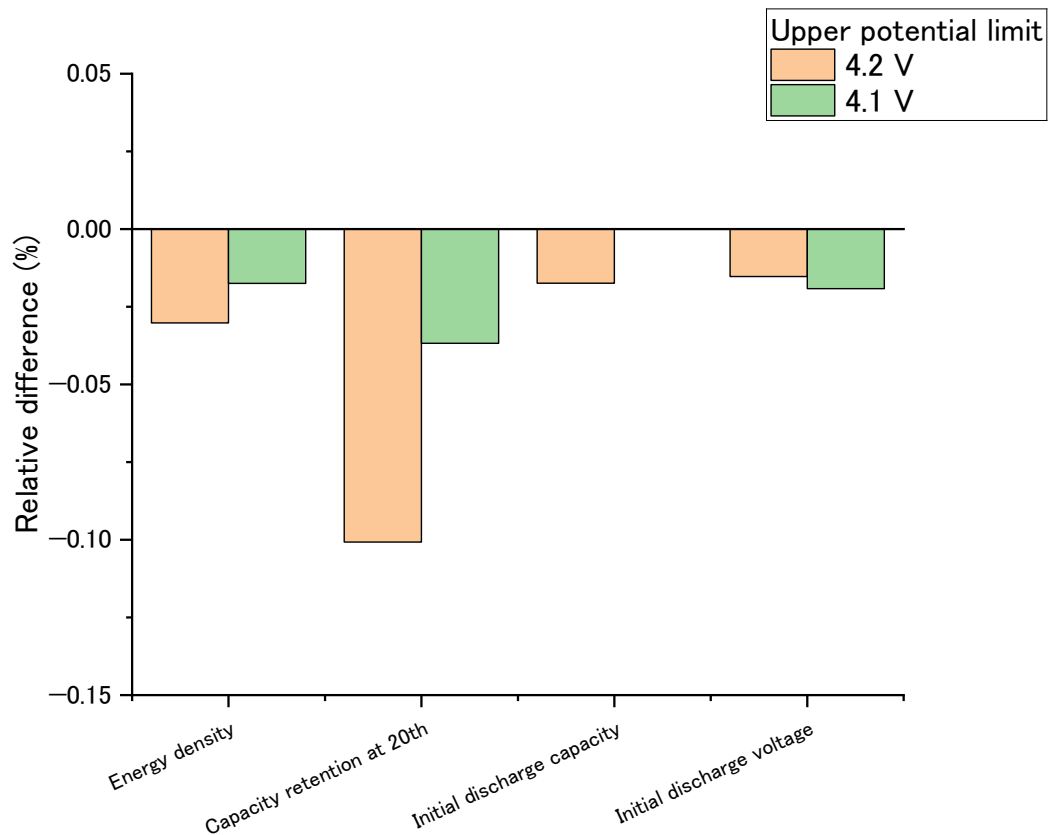|	Energy density (Wh/kg)	Capacity retention (%) (20th)	Initial discharge capacity (mAh g-1)	Average discharge voltage (V)
Pred.2.0 V-4.2 V	563	92.3	172	3.28
Pred.2.0 V-4.1 V	457	92.5	146	3.13
Exp.2.0 V-4.2 V	546	83.0	169	3.23
Exp.2.0 V-4.1 V	449	89.1	146	3.07

Figure S7 Relative difference between predicted and measured values of MNTF.
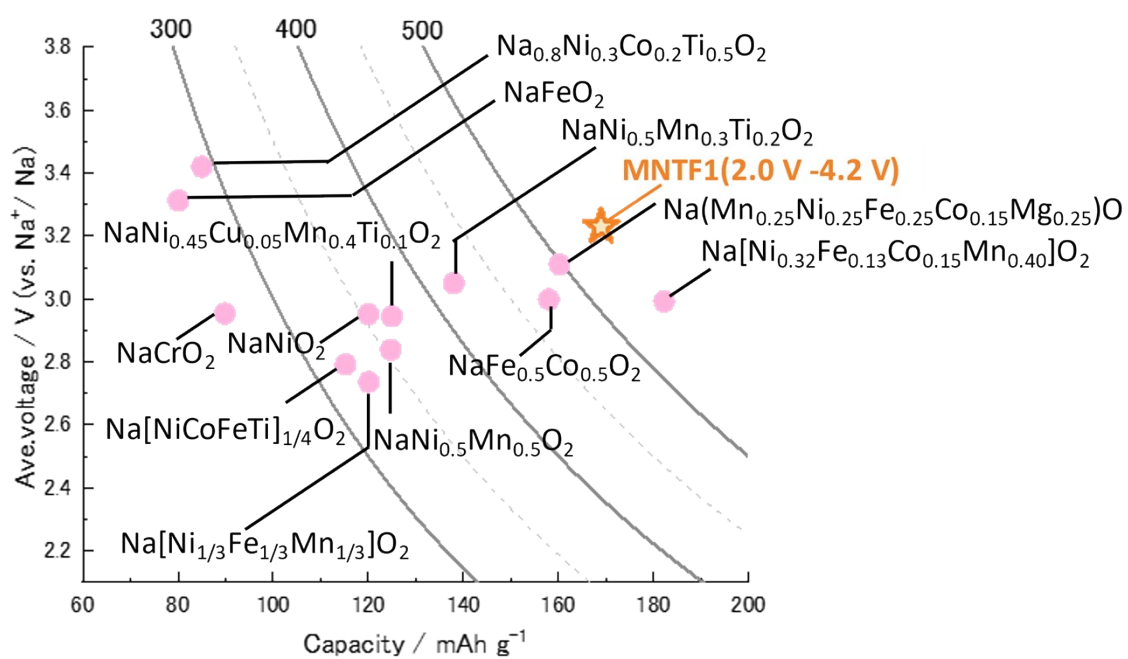
Figure S8 Data from previous report on $NaMeO_2$[1]

1. N. Tapia-Ruiz et al., *J. Phys. Energy*, **3**, 031503 (2021).

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