

1 **SUPPLEMENTARY INFORMATION**

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4 **The role of OOH binding site and Pt surface structure on ORR activities**

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**Table S1: Symbol translation table**

Catalyst symbol used here	Catalyst symbol used in Ref. 40 (Page 7)	Pre-cursor	Dealloying gaseous environment	De-alloying acid	Post annealing <sup>2</sup>
ANAu	176NA	PtNi <sub>3</sub>	Air	HNO <sub>3</sub>	No
N <sub>2</sub> NAu	280NA	PtNi <sub>3</sub>	N <sub>2</sub>	HNO <sub>3</sub>	No
N <sub>2</sub> SAu	280SA	PtNi <sub>3</sub>	N <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>	No
N <sub>2</sub> SAa	280SA-AN	PtNi <sub>3</sub>	N <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>	Yes

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**EXAFS analysis**

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**Table S2: Summary of EXAFS results \***

Catalyst symbol	Cycling stage	R <sub>Pt-Pt</sub>	R <sub>Pt-Ni</sub>	R <sub>Ni-Ni</sub>	N <sub>Pt-Pt</sub>	N <sub>Pt-Ni</sub>	N <sub>Ni-Pt</sub>	N <sub>Ni-Ni</sub>	σ <sup>2</sup> <sub>Pt-Pt</sub>	σ <sup>2</sup> <sub>Pt-Ni</sub>	σ <sup>2</sup> <sub>Ni-Ni</sub>	R-factor
		(ΔR = ±0.008Å) <sup>a</sup>			(ΔN = ±0.9) <sup>b</sup>		(ΔN = ±0.5) <sup>b</sup>		(Δσ <sup>2</sup> = ±0.007) <sup>c</sup>			
ANAu	BOL	2.738	2.630	2.572	9.2	0.7	7.5	4.4				0.005
	10 k	2.743	2.650	2.575	9.6	0.6	6.8	4.1	0.005	0.010	0.009	0.007
	30 k	2.748	2.650	2.577	10.3	0.4	5.9	4.7				0.004
N <sub>2</sub> NAu	BOL	2.713	2.611	2.570	8.1	1.8	6.9	5.5				0.007
	10 k	2.724	2.631	2.574	9.1	1.2	6.7	5.5	0.004	0.010	0.011	0.009
	30 k	2.742	2.631	2.543	10.6	0.4	6.3	5.6				0.009
N <sub>2</sub> SAu	BOL	2.696	2.601	2.581	7.3	2.5	4.8	7.7				0.010
	10 k	2.716	2.604	2.574	8.2	2.2	3.8	7.4	0.007	0.005	0.011	0.012
	30 k	2.736	2.600	2.580	9.7	1.3	3.7	7.4				0.008
N <sub>2</sub> SAa	BOL	2.693	2.598	2.578	8.8	2.1	5.2	7.1	0.007	0.005	0.011	0.006
	10 k	2.717	2.600	2.575								
	30 k	2.734	2.604	2.570	10.4	0.9	4.6	6.9	0.007	0.005	0.011	0.010

35 \*All the data were collected at 0.54 V vs RHE (double layer region) in N<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub>  
36 electrolyte except for the Pt L<sub>3</sub> edge data of the 10k-cycled N<sub>2</sub>SAa catalyst that were collected  
37 under *ex situ* conditions (thus only the bond distance values are given). S<sub>0</sub><sup>2</sup> fixed at 0.766 and  
38 0.682 for Pt and Ni, respectively as obtained by fitting the reference foils. Fits were done in R-  
39 space, k<sup>1,2,3</sup> weighting at Pt L<sub>3</sub> and Ni k edges simultaneously. For Pt, 1.1 < R < 3.4 Å and Δk =  
40 2.95 - 12.14 Å<sup>-1</sup> were used; for Ni, 1.2 < R < 3.0 Å and Δk = 1.87 - 11.93 Å<sup>-1</sup> were used. <sup>a,b,c</sup>Values  
41 represent the largest statistical errors of all of the least-squares fits determined by ARTEMIS.

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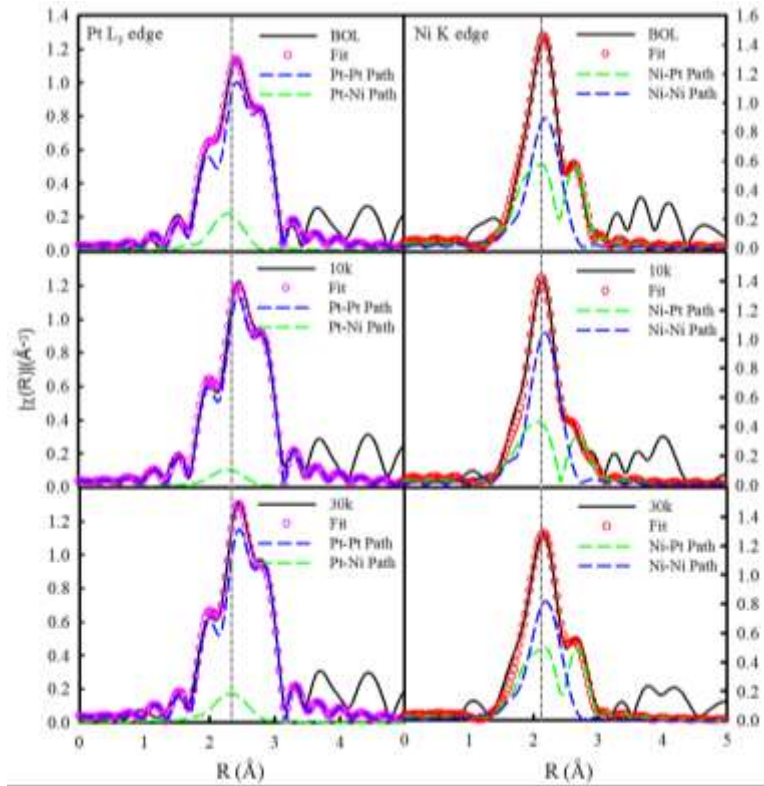
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56 **Figure S1.** Pt L<sub>3</sub> edge (left) and Ni K edge (right) EXAFS spectra collected at 0.54 V in N<sub>2</sub>-  
57 saturated 0.1 M HClO<sub>4</sub> electrolyte and the corresponding least-squares fits for dealloyed PtNi<sub>3</sub>/C  
58 (ANAu) NP catalyst under different voltage cycling stages: BOL (top), 10k (middle), and 30k  
59 (bottom). The vertical black lines are drawn as guides to the eye.

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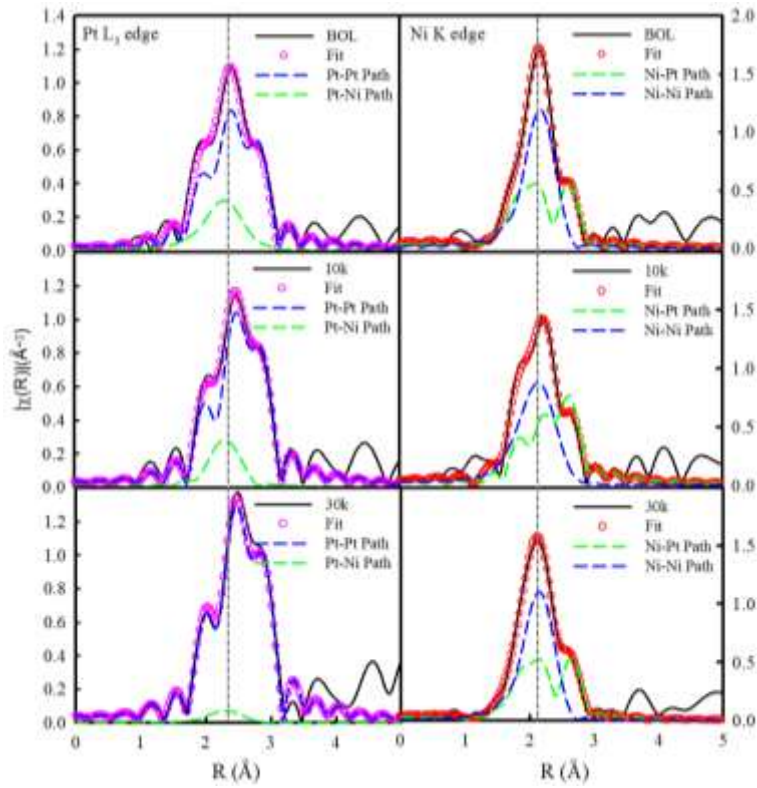
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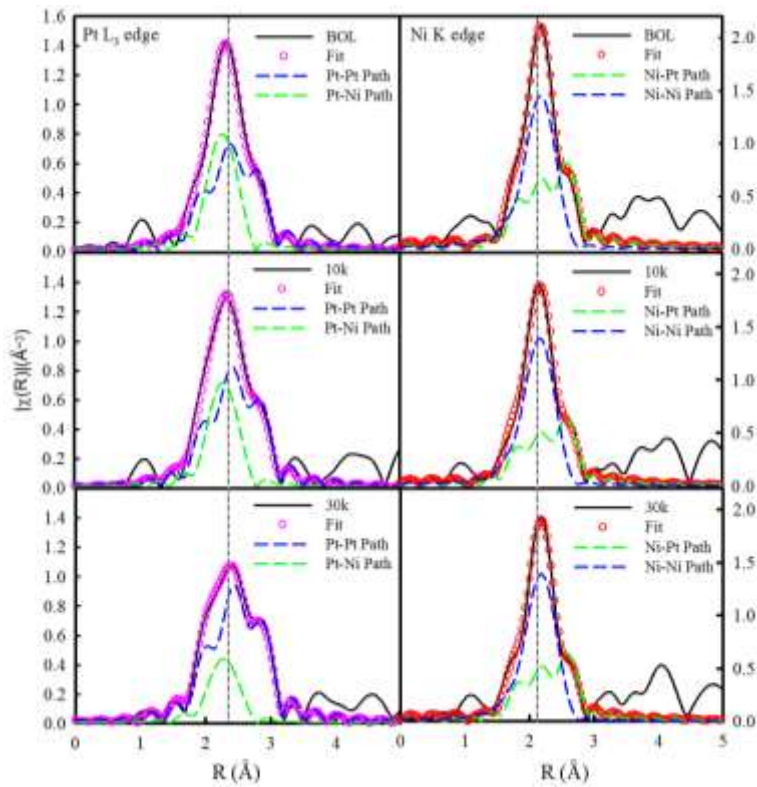


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**Figure S2.** Pt L<sub>3</sub> edge (left) and Ni K edge (right) EXAFS spectra collected at 0.54 V in N<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> electrolyte and the corresponding least-squares fits for dealloyed PtNi<sub>3</sub>/C (N<sub>2</sub>NAu) NP catalyst under different voltage cycling stages: BOL (top), 10k (middle), and 30k (bottom). The vertical black lines are drawn as guides to the eye.

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83 **Figure S3.** Pt L<sub>3</sub> edge (left) and Ni K edge (right) EXAFS spectra collected at 0.54 V in N<sub>2</sub>-  
84 saturated 0.1 M HClO<sub>4</sub> electrolyte and the corresponding least-squares fits for dealloyed PtNi<sub>3</sub>/C  
85 (N<sub>2</sub>SAu) NP catalyst under different voltage cycling stages: BOL (top), 10k (middle), and 30k  
86 (bottom). The vertical black lines are drawn as guides to the eye.

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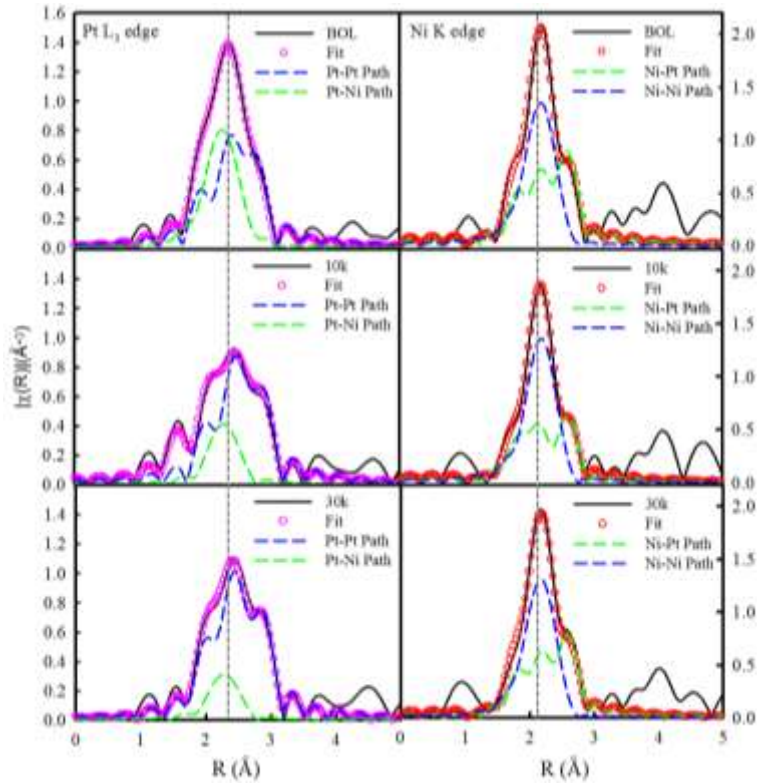
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98 **Figure S4.** Pt L<sub>3</sub> edge (left) and Ni K edge (right) EXAFS spectra collected at 0.54 V in N<sub>2</sub>-

99 saturated 0.1 M HClO<sub>4</sub> electrolyte and the corresponding least-squares fits for dealloyed PtNi<sub>3</sub>/C

100 (N<sub>2</sub>SAA) NP catalyst under different voltage cycling stages: BOL (top), 10k (the Pt L<sub>3</sub> edge data

101 were collected under ex situ condition) (middle), and 30k (bottom). The vertical black lines are

102 drawn as guides to the eye.

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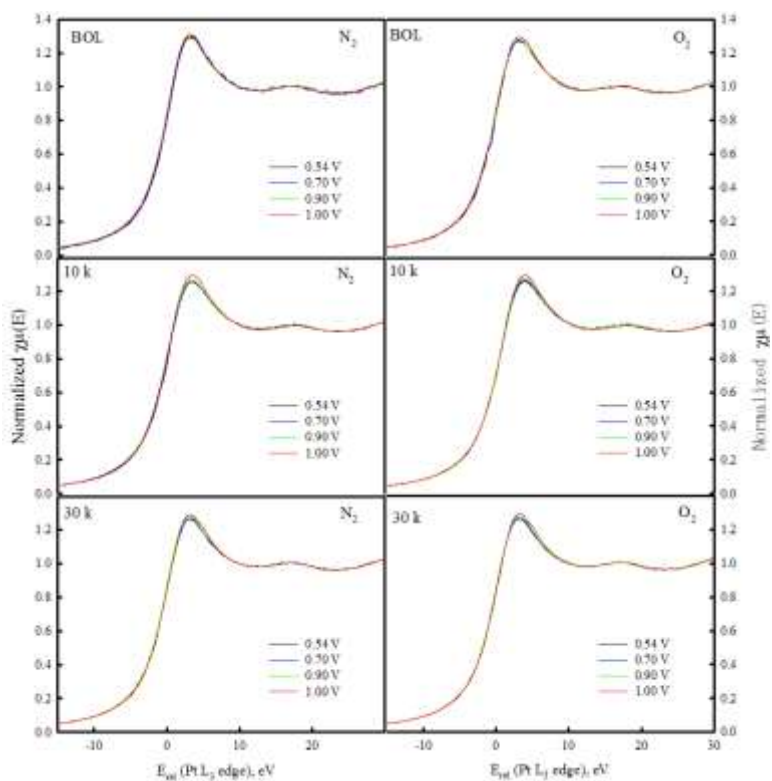
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108 **XANES data**

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111 **Figure S5.** Normalized Pt L<sub>3</sub> edge XANES spectra collected at various potentials in N<sub>2</sub>- (left) or O<sub>2</sub>-  
112 (right) saturated 0.1 M HClO<sub>4</sub> electrolyte for dealloyed PtNi<sub>3</sub>/C (ANAu) NP catalyst under  
113 different voltage cycling stages: BOL (top), 10k (middle), and 30k (bottom).

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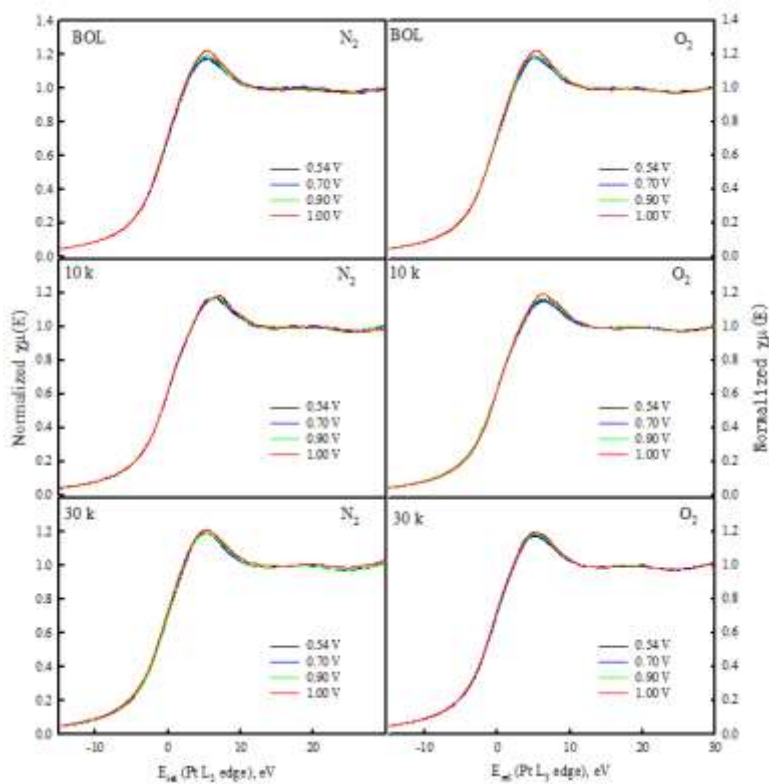
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126 **Figure S6.** Normalized Pt L<sub>3</sub> edge XANES spectra collected at various potentials in N<sub>2</sub>- (left) or O<sub>2</sub>-

127 (right) saturated 0.1 M HClO<sub>4</sub> electrolyte for dealloyed PtNi<sub>3</sub>/C (N<sub>2</sub>NAu) NP catalyst under

128 different voltage cycling stages: BOL (top), 10k (middle), and 30k (bottom).

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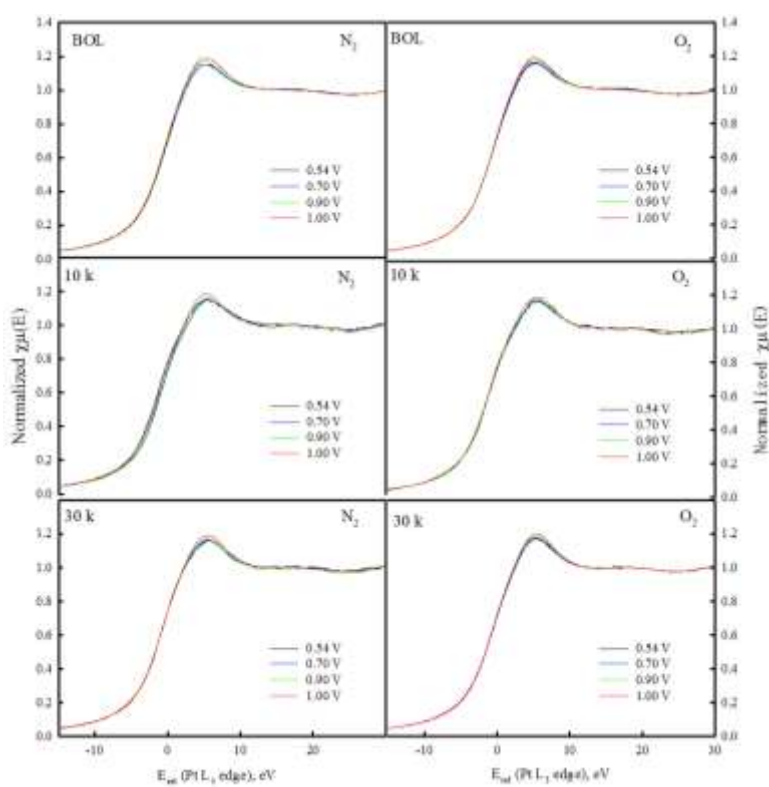
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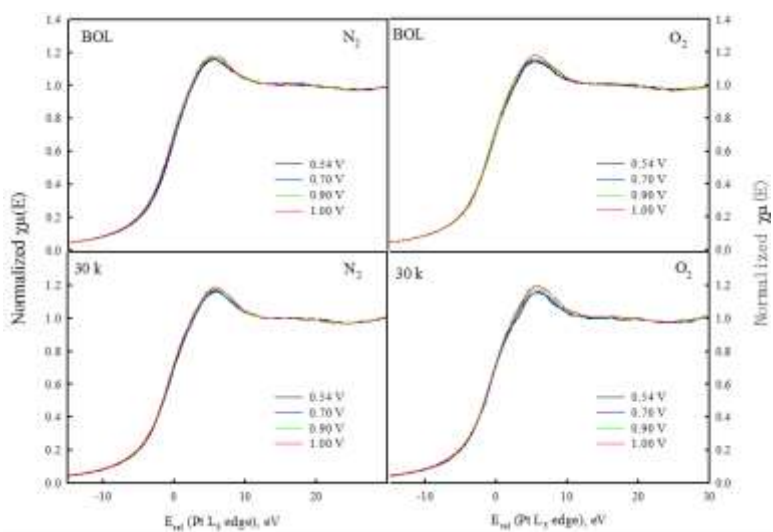
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142 **Figure S7.** Normalized Pt L<sub>3</sub> edge XANES spectra collected at various potentials in N<sub>2</sub>- (left) or O<sub>2</sub>-  
143 (right) saturated 0.1 M HClO<sub>4</sub> electrolyte for dealloyed PtNi<sub>3</sub>/C (N<sub>2</sub>SAu) NP catalyst under  
144 different voltage cycling stages: BOL (top), 10k (middle), and 30k (bottom).

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**Figure S8.** Normalized Pt L<sub>3</sub> edge XANES spectra collected at various potentials in N<sub>2</sub>- (left) or O<sub>2</sub>- (right) saturated 0.1 M HClO<sub>4</sub> electrolyte for dealloyed PtNi<sub>3</sub>/C (N<sub>2</sub>SAA) NP catalyst under different voltage cycling stages: BOL (top) and 30k (bottom).