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# High-rate electrochemical lithium-ion storage through $Li^+$ intercalation pseudocapacitance in $Pr_{1/3}NbO_3$ anode

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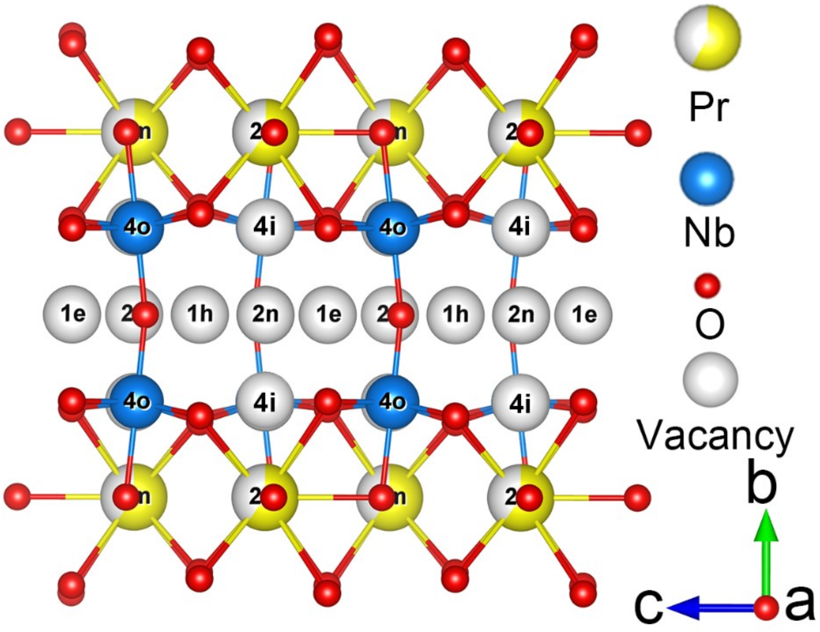

**Fig. S1.** The 1*e*, 1*h*, 2*n* ,2*m*,4*o* and 4*i* sites in $Pr_{1/3}NbO_3$ lattice.

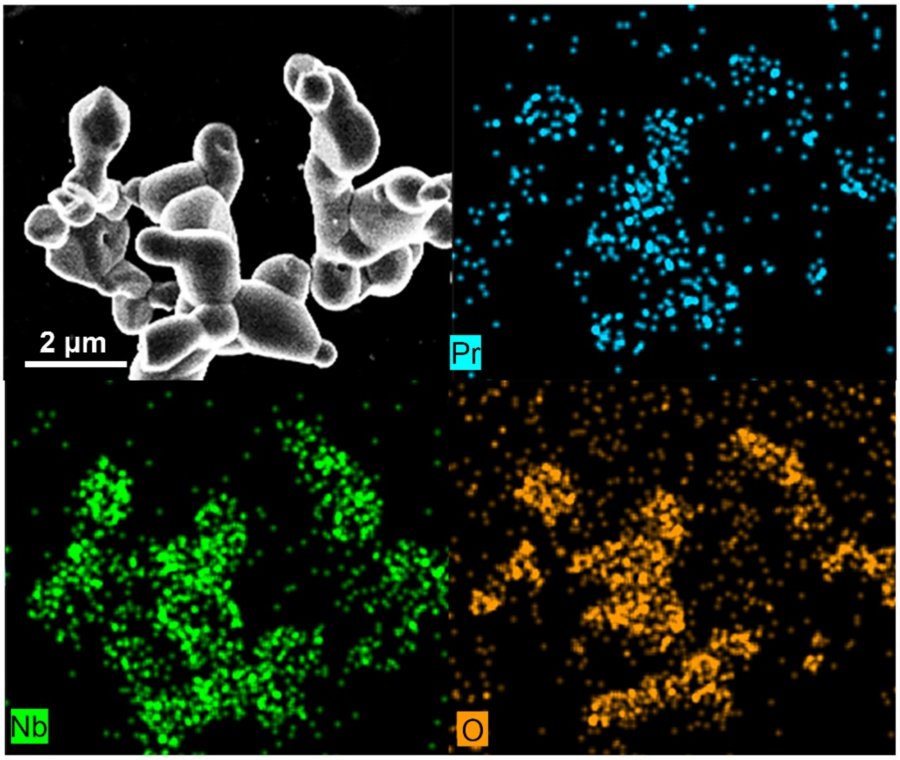

**Fig. S2.** EDS mapping images of Pr, Nb, and O taken from the selected section.

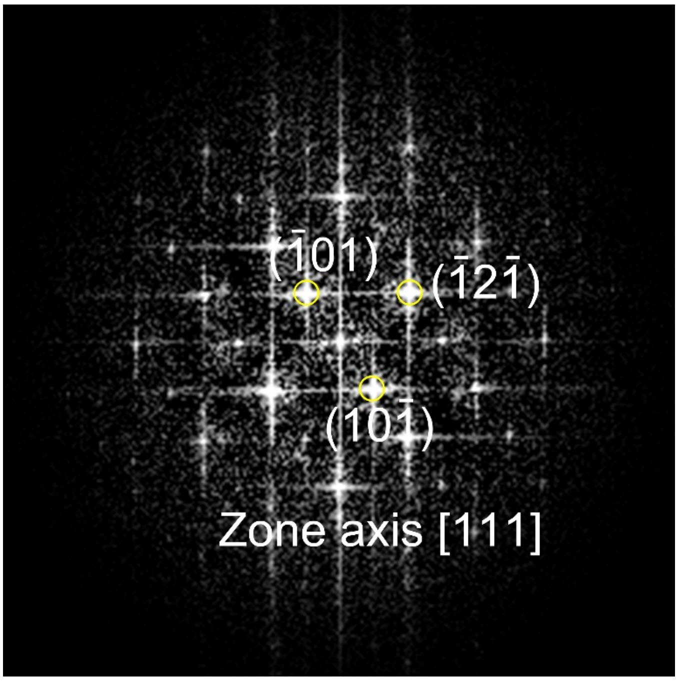

**Fig. S3.** SAED image original from HAADF image of $Pr_{1/3}NbO_3$.

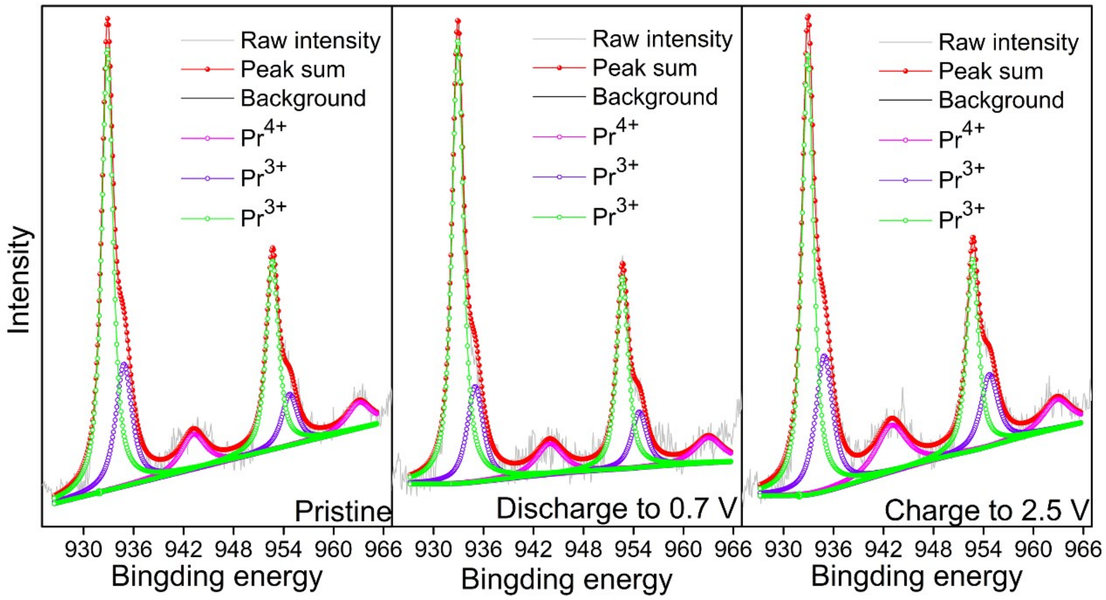

**Fig. S4**. *Ex-situ* Pr-3*d* XPS spectra at different lithiation states.

For pristine $Pr_{1/3}NbO_3$, the peaks at 932.9, 934.9, 952.8, and 954.9 eV are attributed to $Pr^{3+}$ and the peaks at 943.1 and 963.1 eV are ascribed to $Pr^{4+}$ in the Pr-3*d* XPS spectra. During the lithiation and delithiation, no obvious change in the characteristic peaks of $Pr^{3+}$ and $Pr^{4+}$ is detected and no new XPS peaks can be separated from the XPS spectrum of Pr 3*d*. This finding demonstrates that Pr does not undergo redox reactions during the discharge/charge process and does not contribute to the capacity of $Pr_{1/3}NbO_3$.

**Table S1.** Fractional atomic parameters of $Pr_{1/3}NbO_3$ with P2/m space group.

| atom | site | $x$ | $y$ | $z$ | occupancy |
|---|---|---|---|---|---|
| Pr | 2*m* | 0.248232 | 0.0000 | 0.751840 | 0.6667 |
| Nb | 4*o* | 0.253088 | 0.261104 | 0.249832 | 1.000 |
| O1 | 2*n* | 0.240744 | 0.5000 | 0.252841 | 1.000 |
| O2 | 2*m* | 0.220253 | 0 | 0.211661 | 1.000 |
| O3 | 2*l* | 0.5000 | 0.211041 | 0.5000 | 1.000 |
| O4 | 2*k* | 0.0000 | 0.203417 | 0.5000 | 1.000 |
| O5 | 2*j* | 0.5000 | 0.251392 | 0.0000 | 1.000 |
| O6 | 2*i* | 0.0000 | 0.277733 | 0.0000 | 1.000 |

**Table S2**. Lattice parameters of $Pr_{1/3}NbO_3$.

| Sample | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\alpha = \gamma$ (°) | $\beta$ (°) | $V$ (Å$^3$) |
|---|---|---|---|---|---|---|
| $Pr_{1/3}NbO_3$ | 5.518081 | 7.870665 | 5.518272 | 90 | 90.205 | 239.662 |

The$^*$ $R_{wp}$ (weighted profile residual) of $Pr_{1/3}NbO_3$ is 0.1095.

The theoretical capacity of $Pr_{1/3}NbO_3$ is calculated by the following method:

$$Q_{theoretical} = \frac{nF}{3.6M} = \frac{2 \times 96485.3\ C\ mol^{-1}}{3.6\ C\ mA^{-1}h^{-1} \times 187.87\ g\ mol^{-1}} = 285.3\ mAg^{-1}$$

where $n$ is the number of electrons transferred per formula unit, $F$ is Faraday's constant, 3.6 is a conversion factor between coulombs and the conventional milliampere-hour and $M$ is the mass per formula unit. For intercalation Nb-based anode, $Nb^{5+}$ can be reduce to $Nb^{3+}$ with two electron transfer. Therefore, the value of $n$ is 2 in the above equation.

The kinetic analyses of the $Li^+$ storage in $Pr_{1/3}NbO_3$ was conducted using CV tests at various scan rates ranging from 0.2 to 0.5 mV $s^{-1}$. In this case, the pseudocapacitive contribution to the electrochemical capacity can be calculated based on **Equation** (**1**). [S1]

$$i\,(V) = k_a v + k_b v^{1/2} \qquad \textbf{(1)}$$

where, $i$ (V) is the total current at a given voltage, $v$ is the scan rate, and $k_p$ and $k_d$ are adjustable factors. $K_a v$ and $k_b v^{1/2}$ are the currents from the pseudocapacitive contribution and the diffusion-controlled process, respectively.

The $Li^+$ diffusion coefficients ($D_{Li}$) were calculated from GITT data based on **Equation** (2). [S2-S5]

$$D_{Li} = \frac{4}{\pi t}\left(\frac{m_B V_m}{M_B S}\right)^2\left(\frac{\Delta E_S}{\Delta E_\tau}\right)^2 \quad (t \ll L^2/D_{Li}) \qquad \textbf{(2)}$$

where, $m_B$, $M_B$, $V_m$ and $L$ present the mass, molar mass, and molar volume, of the active material, respectively; $S$ is the surface area and linear length of the working electrode; $t$ is the time during which a constant current is applied; $\Delta E_S$ and $\Delta E_\tau$ respectively embody the change in the equilibrium voltage and the change in voltage during the current pulse. Based on **Equation** (2) the apparent $Li^+$ diffusion coefficients of $Pr_{1/3}NbO_3$ during different discharge/charge states are obtained and displayed in **Fig. 4f**.

**Table S3.** Comparisons of average $Li^+$ diffusion coefficients ($D_{Li}$) of $Pr_{1/3}NbO_3$ with those of fast charging anode materials previously reported. The $Li^+$ diffusion coefficients were calculated through GITT.

| material | $D_{Li}$ ($cm^2\ s^{-1}$) | reference |
|---|---|---|
| $Pr_{1/3}NbO_3$ | $1.78\times10^{-11}$ | This work |
| $Cu_2Nb_{34}O_{87}$ | $3.5\times10^{-13}$ | S6 |
| $MoNb_{12}O_{33}$ | $3.9\times10^{-14}$ | S7 |
| $Al_{0.5}Nb_{24.5}O_{62}$ | $1.65\times10^{-12}$ | S8 |
| $TiNb_2O_7$ | $4.28\times10^{-14}$ | S9 |
| $Zn_2Nb_{34}O_{87}$ | $5.6\times10^{-12}$ | S10 |
| $Li_4Ti_5O_{12}$ | $3.27\times10^{-12}$ | S11 |
| $HfNb_{24}O_{62}$ | $1.51\times10^{-13}$ | S12 |

Figure 4a illustrates the CV curves of the $Pr_{1/3}NbO_3$||Li half cell at 0.2, 0.3, 0.4 and 0.5 mV $s^{-1}$, respectively. It is found from Figure 4d that the cathodic/anodic peak current ($I$p) during the intensive $Nb^{4+}/Nb^{5+}$ redox reactions delivered a linear relationship with the square root of the sweep rate ($v^{0.5}$). Therefore, the $Li^+$ diffusion coefficients ($D_{Li}$) of $Pr_{1/3}NbO_3$ can be calculated based on the Randles– Sevick Equation (3): S13

$$I_p = 2.69\times10^5 \times n^{1.5}CSD_{Li}^{0.5}\ v^{0.5} \tag{3}$$

where $n$ is the charge transfer number, $S$ is the surface area of the electrode, and $C$ is the allowed $Li^+$ molar concentration in $Pr_{1/3}NbO_3$ crystals. The calculated apparent $Li^+$ diffusion coefficients of $Pr_{1/3}NbO_3$ are $2.83\times10^{-11}$ (lithiation) and $4.01\times10^{-11}$ $cm^2\ s^{-1}$ (lithiation).

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