Mitigating Jahn–Teller Effect of MnO2 viaCharge Regulation of Mn-Local Environment for Advanced Calcium Storage

**Experimental Procedures**

**1 Synthesis of the MnO2**

MnO2 was synthesized by a facile hydrothermal method[1]. First, 400 mg KMnO4 was dissolved in 40 mL deionized water with stirring at room temperature for 5 minutes. Then, add 78.3 mg of MnSO4∙H2O to the above solution and stirred at room temperature for 1 hour. The mixture solution was transferred into a 50 mL Teflon-lined autoclave and keep it at 160°C in an oven for 16 hours. Wash the product three times with deionized water. Finally, the MnO2 was acquired through the freeze-drying.

**2 Synthesis of the Mo-MnO2**

The synthesis of Mo-MnO2 involves adding varying amounts of (NH4)6Mo7O24·4H2O into the solution for synthesizing MnO2, with continuous stirring. The resulting samples are named MMO-20 (20mg), MMO-40 (40mg), MMO-60 (60mg) and MMO-80 (80mg), respectively.

**3 Materials Characterizations**

The crystal structure and morphology of the samples were characterized using X-ray diffraction (XRD) (D8 Advance, Bruker AXS GmbH, Karlsruhe, Germany) and scanning electron microscopy (SEM, JEOL-7100F). The morphology was also examined using transmission electron microscopy (TEM) and high-resolution TEM images obtained from TEM, JEM-2100F. Infrared spectra were collected using a Nicolt iS50 spectrometer. Thermogravimetric analysis (TGA) was performed on a NETZSCH-STA449c/3/G thermal analysis instrument with a temperature range of 30-600°C. XPS spectroscopy measurements were conducted using the AXIS SUPRA. The discharged electrode samples were tested using a time-of-flight secondary ion mass spectrometer (nano TOFII). Raman spectra were collected using a Raman spectrometer (LabRAM HR Evolution & SmartSPM). The electrochemical performance, including specific capacity, rate capability, and cycling performance, was evaluated using a Neware battery testing system (BTS80) with a constant current charge-discharge method.

**4 Electrochemical Measurements**

After thoroughly mixing 60 wt% of active material, 30 wt% of Ketjen Black, and 10 wt% of binder (polytetrafluoroethylene, PTFE), the working electrode was pressed. The mass loading of the cathode electrode is approximately~1.5 mg cm-2. It was dried under vacuum at 60°C for 12 hours. The electrochemical performance was tested using a CR2016 coin cells in a glovebox filled with argon (<0.1 ppm of H2O and <0.5 ppm of O2). The anode electrode used active carbon (AC), and a glass fiber membrane (GF/A What-man) was employed as the separator. The 0.5 M Ca(TFSI)2/AN serves as the electrolyte. Ca(TFSI)₂ has been widely reported as an electrolyte for CIBs for several key reasons[2]: a wide electrochemical stability window, high ionic conductivity, and low viscosity. These characteristics make Ca(TFSI)₂ an attractive choice for the development of CIBs.Galvanostatic charge–discharge measurements and galvanostatic intermittent titration technique (GITT) tests were conducted on a multi-channel battery testing system (CT2001A, LAND, Wuhan, China). According to our previous work, the potential of the alternating electrode can be calculated to be approximately 3.023 V vs. Ca/Ca2+[3]. The current pulse was set to 50 mA g−1, applied for 10 minutes, and then rested for 30 minutes to obtain the GITT curve. In-situ XRD measurements were performed between 20° and 45° using a stainless steel open-type coin cell connected to a multi-channel battery testing system (Neware, China). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) plots were collected using a VMP3 multichannel electrochemical workstation (Bio-Logic France).

**5 Computational details**

Density functional theory (DFT) calculations were performed using the projector augmented-wave (PAW) method, as implemented in the Vienna Ab initio Simulation Package (VASP)[4]. The exchange-correlation functional was treated within the generalized gradient approximation (GGA), utilizing the Perdew-Burke-Ernzerhof (PBE) scheme[5]. The plane-wave basis set was truncated at a cutoff energy of 500 eV, and the energy convergence criterion for the self-consistent field iterations was set to 10-5 eV. For Brillouin zone integration, a k-point mesh was generated with a spacing of 0.040 Å, ensuring comprehensive sampling. All structures underwent full relaxation until the forces on each atom were diminished to below 0.03 eV/Å. Furthermore, the DFT-D3 correction method was incorporated to accurately account for weak van der Waals interactions[6]. Charge transfers between Ca2+ and the host structure were analyzed using Bader charge analysis. To investigate the migration pathway and energy barriers of Ca2+ ions, we employed the Climbing Image Nudged Elastic Band (CI-NEB) method.

The vacancy formation energy for Mn in MnO2 is defined as

Here, and denote the total energies of MnO2 with a single Mn vacancy and the perfect MnO2 crystal, respectively, while represents the chemical potential of Mn. The doping formation energy for doping Mo atom into MnO2 is categorized into four scenarios:

Without Mn vacancy, and one Mo atom is doped interlayer

Without Mn vacancy, and one Mn atom of layer is replaced by Mo atom

With one Mn Vacancy, and one Mo atom is doped interlayer

With one Mn vacancy, and the Mn vacancy is occupied by Mo atom

Here, and respectively represent the total energy of Mo atom doped into the interlayer of MnO2 without Mn vacancy and into the interlayer of MnO2 with one Mn vacancy. , and denote the total energy of the perfect MnO2 structure, the total energy of MnO2 with a single Mn vacancy and Mo atom replace the Mn atom. and represent the chemical potential of Mn and Mo atom, respectively.

**6 Capacitive capacity contribution calculation**

According to previous reports[7], the peak current (*i*) and the sweep rate (*v*) meet the empirical formula *i* =*av*b, where a and b are adjustable parameters. Furthermore, the contributions of diffusion controlled and capacitive process can be determined by the following equation,

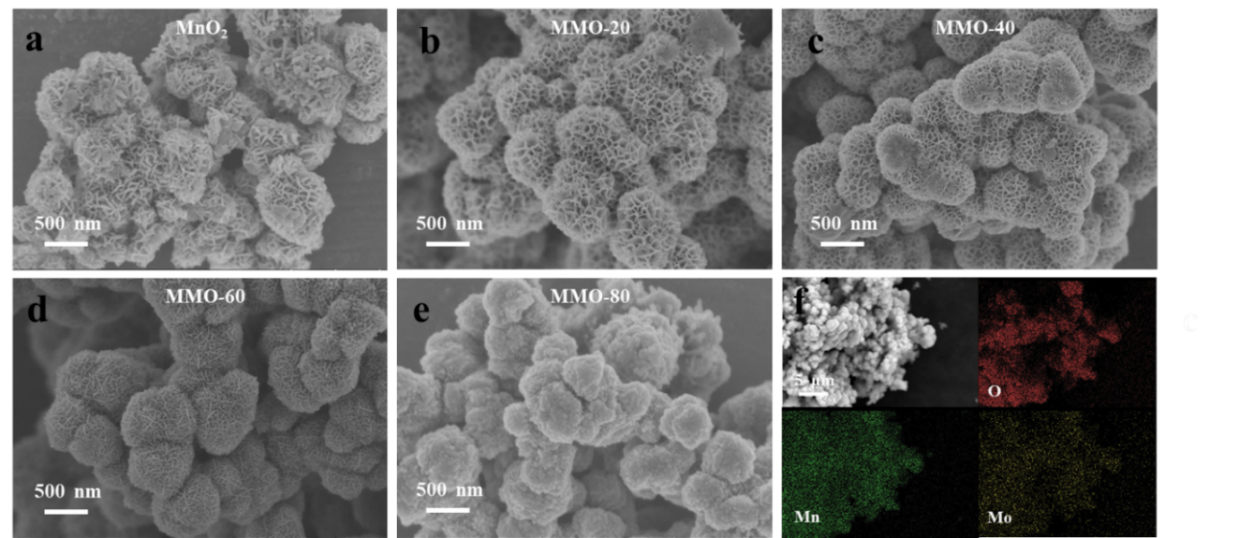
*i*(V) = *k*1v + *k*2*v*1/2  (1)

where *i* is the current (A g−1), *v* is the scan rate (mV s−1).

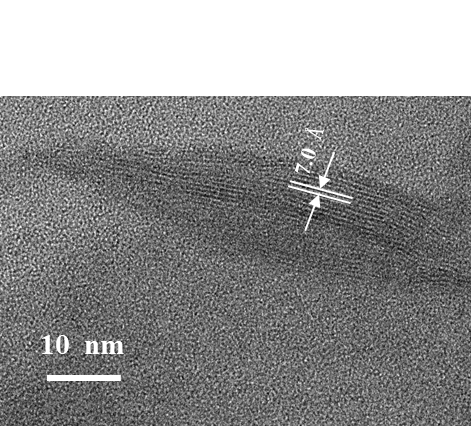
**7 Supplementary Figures and Tables**

**Table S1**. Electrochemical performances of reported cathodes for CIBs and the MMO-40 cathode in non-aqueous electrolyte (AC as counter electrode)

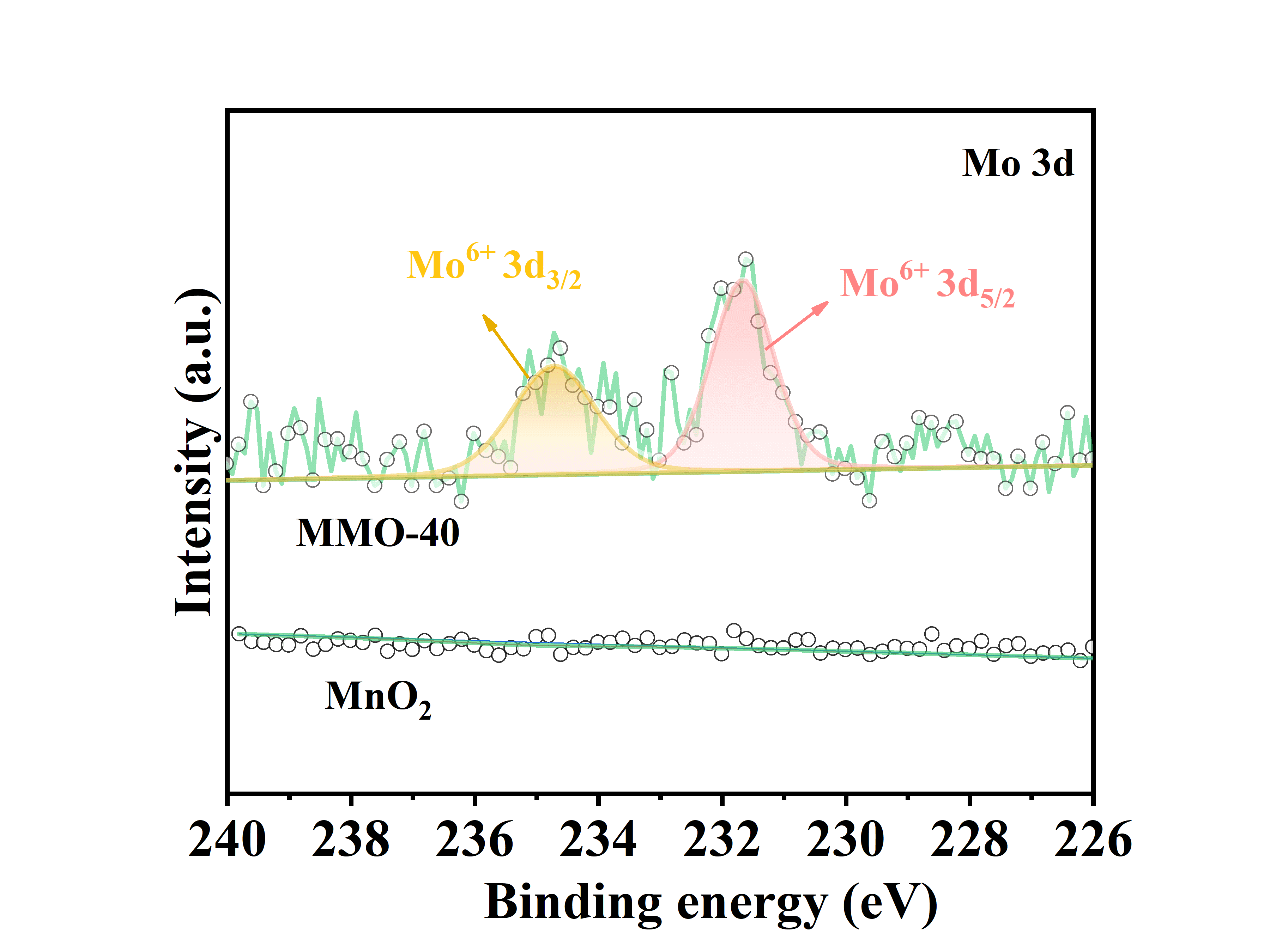
|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Materials | Electrolyte | Counter electrode | Operation range (V)  versus Ca/Ca2+ | specific capacity/current density (mA h g-1) | Voltage(V) | References |
| **MMO-40** | **Ca(TFSI)2/AN** | **AC** | **1.4 – 4.4 V** | **148/100 135/200 130/500 129/1000** | **0.2 V** | **This Work** |
| Mg0.25V2O5·H2O | Ca(TFSI)2 EC/PC/EMC/DMC | AC | 1.4 – 4.1 V | 120/20 90/50 72/100 | -0.15 V | [8] |
| VOPO4·2H2O | Ca(TFSI)2 EC/PC/EMC/DMC | AC | 0.9 – 4.2 V | 120/10 100/20 70/50 55/100 40/200 | 0.5 V | [9] |
| NaV2(PO4)3 | Ca(BF4)2 EC/PC | AC | 2.8 – 3.5 V | 72/5.8 70/11.7 65/23.4 58.8/58 53/117 | 0.4 V | [10] |
| CaxNa0.5VPO4.8F0.7 | Ca(PF6)2 | AC | 1.9 – 4.3 V | 88/10 82/20 72/50  62/100 53/200 42/500 | 0.5V | [11] |
| Na1V2(PO4)2F3 | 0.5 M Ca(PF6)/ EC/PC/EMC/DMC | AC | 2.8 – 4.4 V | 110/5 108/10 105/20  90/100 82/200 56/500 | 0.6 V | [12] |
| CaMn2O4 | Ca(TFSI)2/DME | AC | 1.7 –3.8 V | 60/50 | 0.15 V | [13] |
| MnO2-P | Ca(TFSI)2/AN | AC | 1.4 – 4.4 V | 140/100 140/200 134/500  129/1000 | 0.1 V | [14] |
| δ-MnO2 | Ca(TFSI)2/AN | AC | 1.4 – 4.4 V | 130/100 120/200 105/500 | 0.15 V | [15] |
| Cr-NH4V4O10 | Ca(TFSI)2/PC | AC | 2.37 – 3.52 V | 80/50 70/100 65/150  62/200 60/300 50/500 | -0.4 V | [16] |
| K0.31MnO2·0.25H2O | Ca (NO3)2∙4H2O/H2O | AC | 2.27 – 3.87 V | 84/25 | 0.1 | [17] |
| CaV6O16·2.8H2O | Ca(TFSI)2/DME | AC | 1.4 – 2.2 V | 170/50 134/100 104/500 | -0.6 V | [15] |
| β-Ag0.33V2O5 | Ca(PF6)2 EC/PC | AC | 1.87 – 3.87 V | 179/12.3 | -0.4 V | [18] |

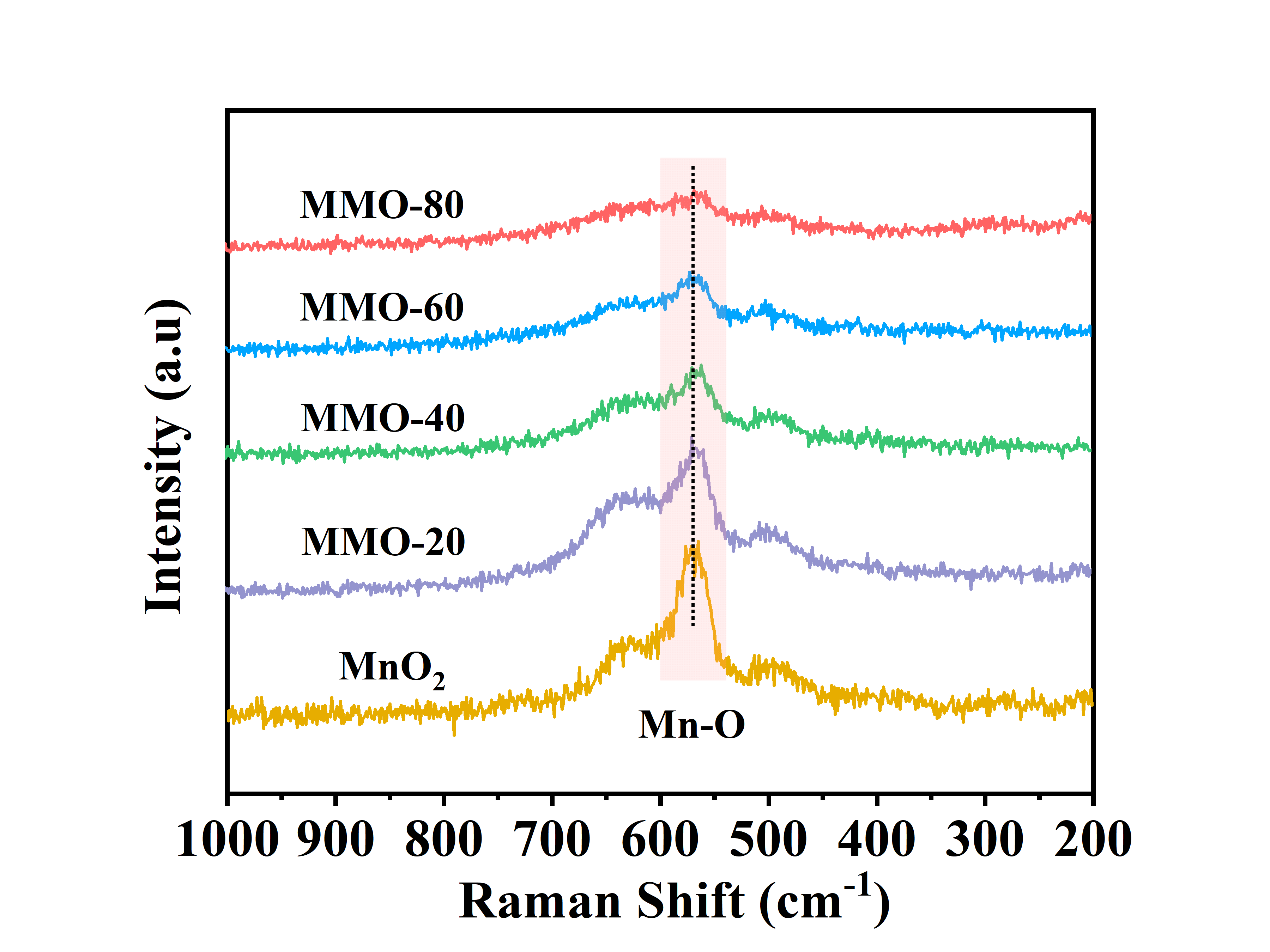
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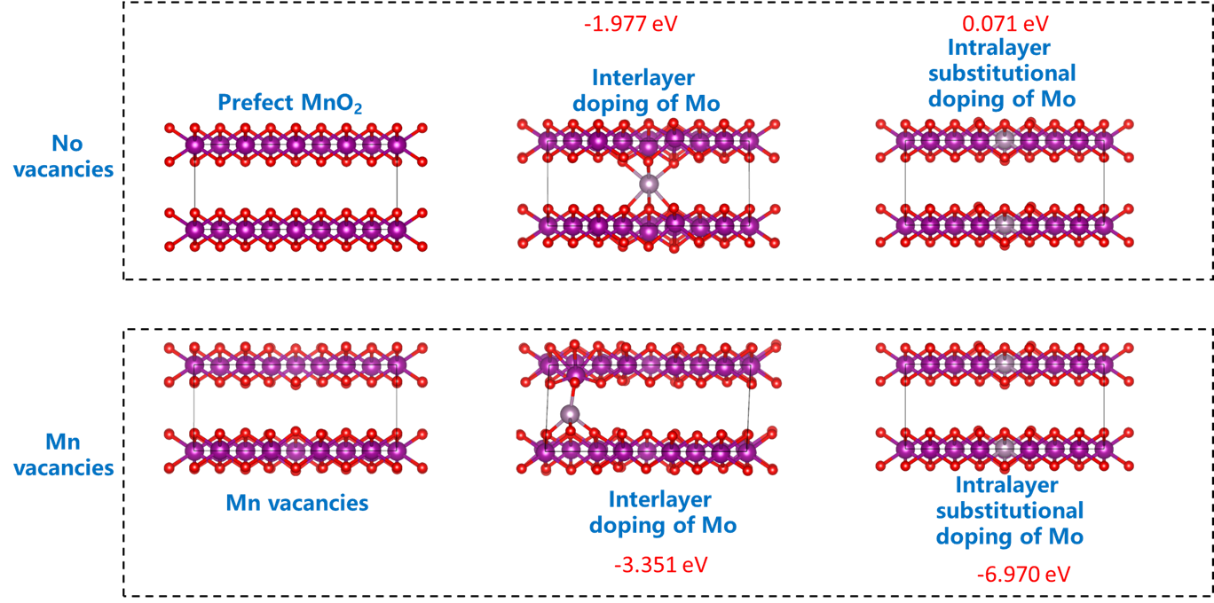
**Figure S1.** (a-e) The SEM image of pristine MnO2 and MMO-20, MMO-40, MMO-60, and MMO-80; (f) The EDS mapping images of MMO-40.



**Figure S2.** The HRTEM image of MnO2.



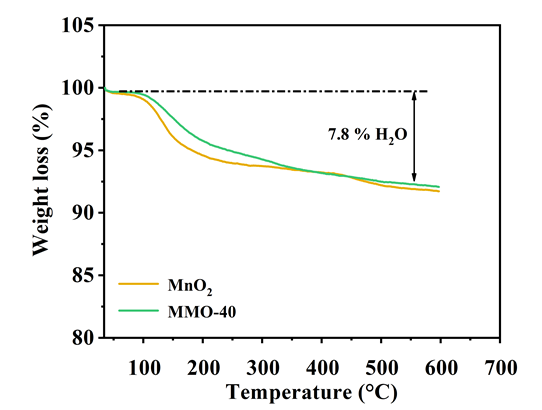
**Figure S3.** Mo 3d XPS spectra of pristine MnO2 and MMO-40.  


**Figure S4.** Raman spectra of pristine MnO2 and MMO-20, MMO-40, MMO-60, and MMO-80.   


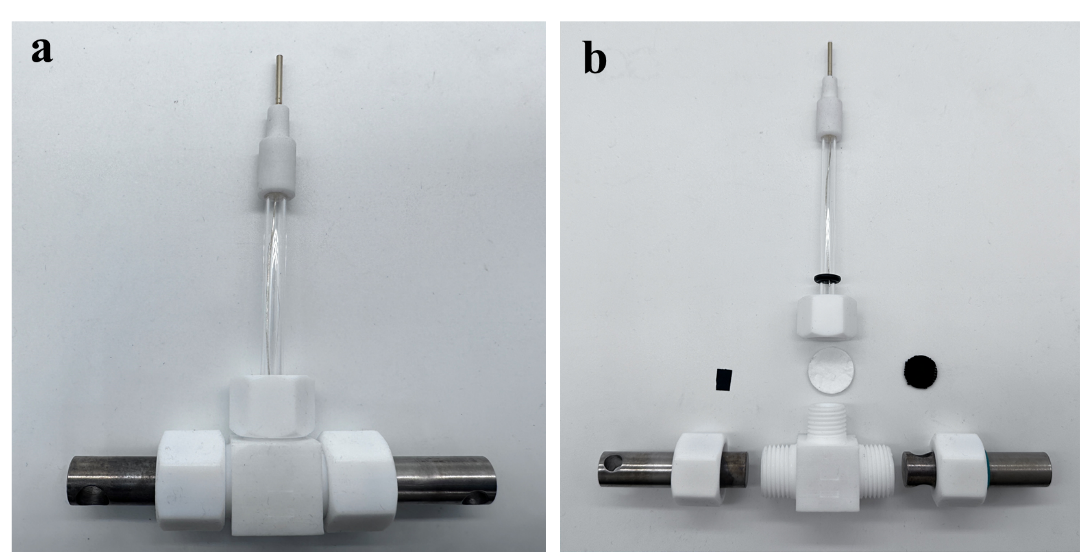
**Figure S5.** In a perfect MnO2 crystal, Mo atoms are more easily doped into the interlayer; In the case of Mn defects, Mo atoms are more easily doped into Mn vacancies

**Table S2.** The ICP result of MnO2, MMO-20, MMO-40, MMO-60 and MMO-80.

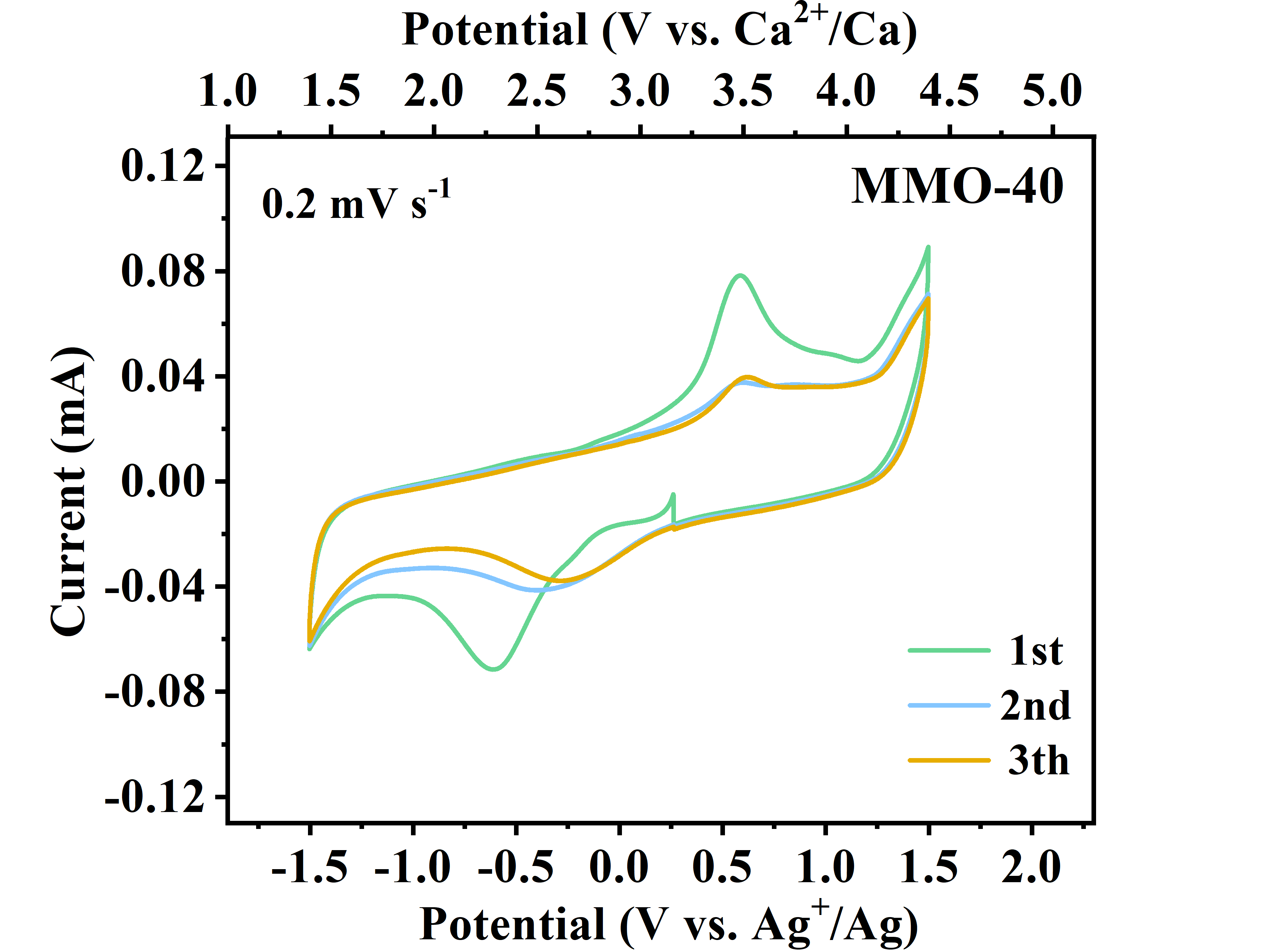
|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sample**  **Element** | MnO2 | MMO-20 | MMO-40 | MMO-60 | MMO-80 |
| K | 10.86 | 11.20 | 10.85 | 9.31 | 8.48 |
| Mn | 48.42 | 43.62 | 45.84 | 43.3 | 44.04 |
| Mo | 0.002 | 0.29 | 2.02 | 2.53 | 3.46 |



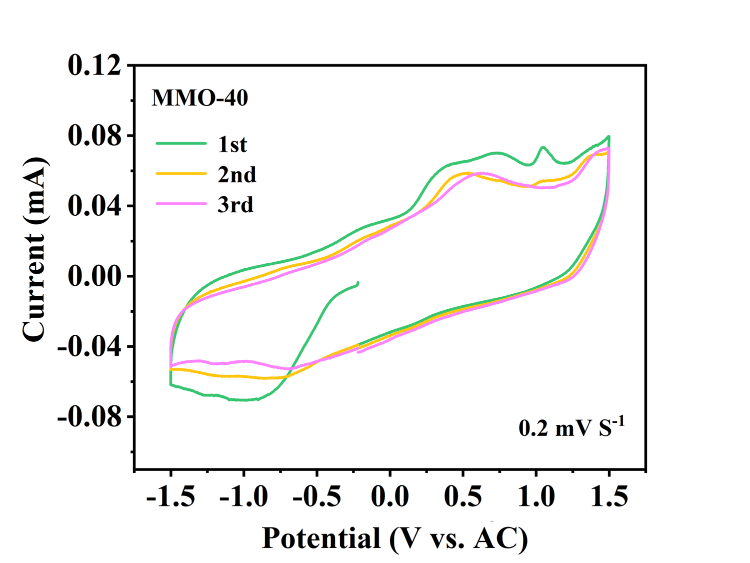
**Figure S6.** The TG curve of pristine MnO2 and MMO-40.



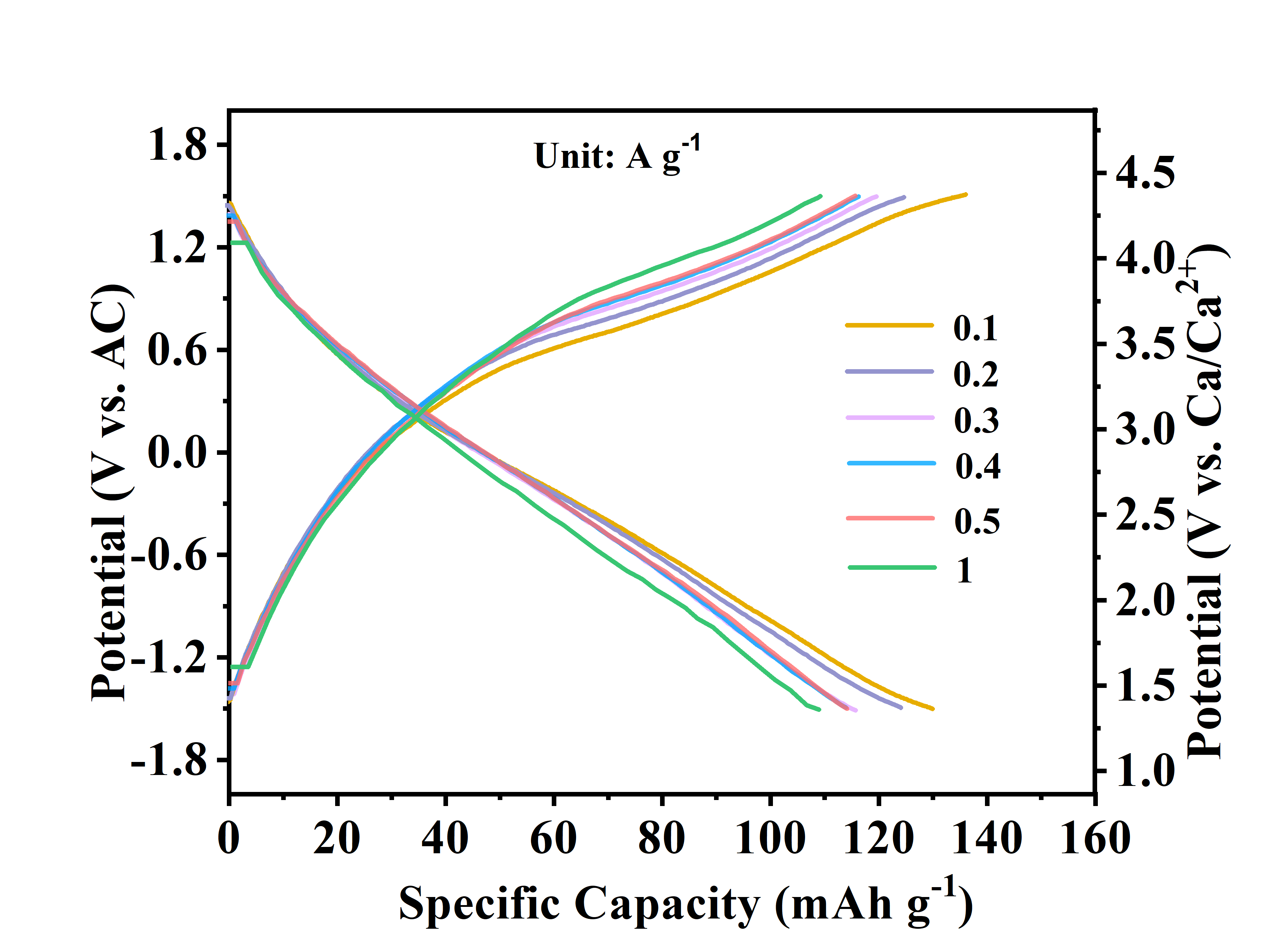
**Figure S7**. (a) The photograph of the Swagelok-type cell. (b) The photograph of each part for the assembly of Swagelok-type cell.

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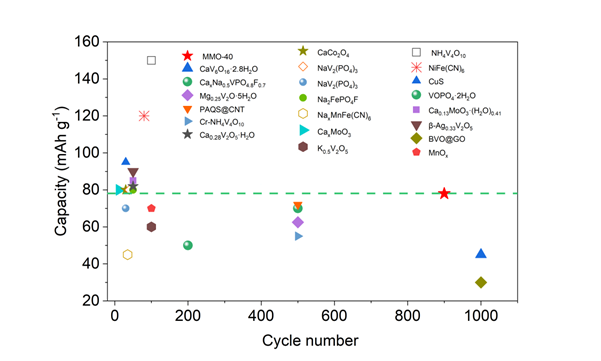
**Figure S8.** The CV curves of MMO-40 in Swagelock-type battery.



**Figure S9.** The CV curves of MMO-40.



**Figure S10.** The GCD profiles of MMO-40 at current densities ranging from 0.1 to 1.0 A g−1.

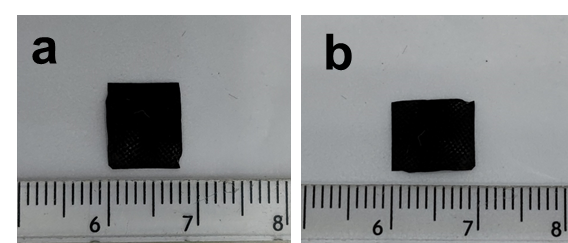


**Figure S11.** Comparison of rate capability and cycle stability of different materials used in CIBs.

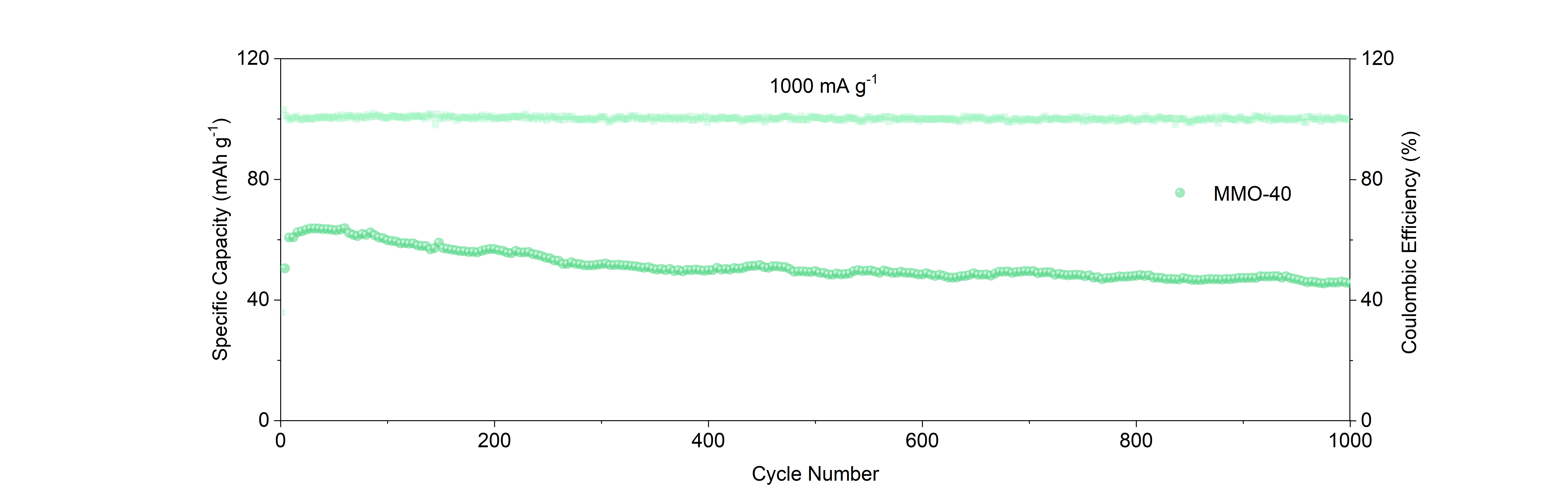
**Table S3**. Electrochemical performances of reported cathodes for CIBs and the MMO-40 cathode in non-aqueous electrolyte

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Materials | Electrolyte | Counter electrode | Operation range (V)  versus Ca/Ca2+ | Specific capacity/current density (mA h g-1) | Cycling performance after n cycle at z (mA h g-1/mA g-1) | References |
| **MMO-40** | **Ca(TFSI)2/AN** | **AC** | **1.4 – 4.4 V** | **140/100 124/200 117/300 115/300 114/500 112/1000** | **~ 78 after 1000 cycles (z=1000)** | **This Work** |
| δ-MnO2 | Ca(TFSI)2/AN | AC | 1.4 – 4.4 V | 130/100 120/200 105/500 88/1000 | ~ 80 after 50 cycles (z=500) | [19] |
| MnOx | Ca(TFSI)2/AN | AC | 1.47 – 3.87 V | 133/11.2 | ~ 70 after 100 cycles | [20] |
| CaV6O16·2.8H2O | Ca(TFSI)2/DME | AC | 1.4 – 2.2 V | 170/50 134/100 104/500  47/800 | ~ 45 after 1000 cycles  (z=500) | [21] |
| Mg0.25V2O5·H2O | Ca(TFSI)2 EC/PC/EMC/DMC | AC | 1.4 – 4.1 V | 120/20 90/50 72/100 | ~ 62.5 after 500 cycles | [22] |
| K0.5V2O5 | Ca(ClO4)2/PC | AC | 2 – 4.3 V | 50/133 | ~60 after 100 cycles | [23] |
| NH4V4O10 | Ca(ClO4)2 AN | AC | 2.6 – 3.9 V | 150/100 90/300 65/500 61/1000 | ~ 150 after 100 cycles (z=100) | [24] |
| VOPO4·2H2O | Ca(TFSI)2 EC/PC/EMC/DMC | AC | 0.9 – 4.2 V | 120/10 100/20 70/50 55/100 40/200 | ~ 50 after 200 cycles | [25] |
| Cr-NH4V4O10 | Ca(TFSI)2/PC | AC | 2.37 – 3.52 V | 80/50 70/100 65/150  62/200 60/300 50/500 | ~ 55 after 500 cycles | [26] |
| Ca0.28V2O5·H2O | Ca(ClO4)2/PC | AC | 1.67 – 4.07 V | 138/10 122/20 110/30  90/50 | ~ 82 after 50 cycles | [27] |
| β-Ag0.33V2O5 | Ca(PF6)2 EC/PC | AC | 1.87 – 3.87 V | 179/12.3 | ~ 90 after 50 cycles | [28] |
| CaxNa0.5VPO4.8F0.7 | Ca(PF6)2 | AC | 1.9 – 4.3 V | 88/10 82/20 72/50  62/100 53/200 42/500 | ~ 70 after 500 cycles | [29] |
| CaCo2O4  NaV2(PO4)3  NaV2(PO4)3  Na2FePO4F | Ca(ClO4)2/AN  Ca(TFSI)2/AN  Ca(BF4)2 EC/PC  Ca(PF6)2 EC/PC | Ag/Ag+  AC  AC  AC | 2.65 – 3.65 V  2.5 – 3.3 V  2.8 – 3.5 V  1.4 – 5 V | 50/0.03 70/0.04 80/0.1    80/7.5  72/5.8 70/11.7 65/23.4 58.8/58 53/117  70/10 | ~ 80 after 30 cycles  ~ 80 after 40 cycles  ~ 70 after 30 cycles  ~ 80 after 50 cycles | [30]  [31]  [32]  [33] |
| NiFe(CN)6 | Ca(PF6)2 EC/PC | AC | 2.1 – 3.97 V | 100/18 90/36 65/72 | ~ 120 after 80 cycles | [34] |
| NaxMnFe(CN)6 | Ca(PF6)2 EC/PC | CaxSn | 1.8 – 5.8 V | 10/100 | ~ 45 after 35 cycles | [35] |
| Ti2O(PO4)2(H2O) | Ca(PF6)2 EC/PC | AC | 1.87 – 3.87 V | 86/20 60/50 38.5/100  17.2/200 | ~ 60.8 after 1500 cycles | [36] |
| BVO@GO | Ca(TFSI)2 EC/PC/EMC/DMC | AC | 1.4 – 4.4 V | 170/300 | ~ 30 after 1000 cycles | [37] |
| PAQS@CNT | Ca(TFSI)2 EC/PC/EMC/DMC | Ag/Ag+ | 1.27 – 3.72 V | 118/50 115/100 90/200  85/500 78/1000 70/2000  60/4000 | ~ 72 after 500 cycles | [38] |
| α-MoO3 | Ca(TFSI)2/AN | AC | 2.07 – 3.37 V | 150/20 125/40 98/80  80/120 60/200 | ~ 100 after 500 cycles | [39] |
| Ca0.13MoO3·(H2O)0.4 | Ca(ClO4)2/AN | AC | 1.67 – 3.87 V | 192/85 138/171 108/342 | ~ 85 after 50 cycles | [40] |
| CuS | Ca(TFSI)2 EC/PC/EMC/DMC | AC | 1.5 – 3.2 V | 200/100 | ~ 95 after 30 cycles | [41] |

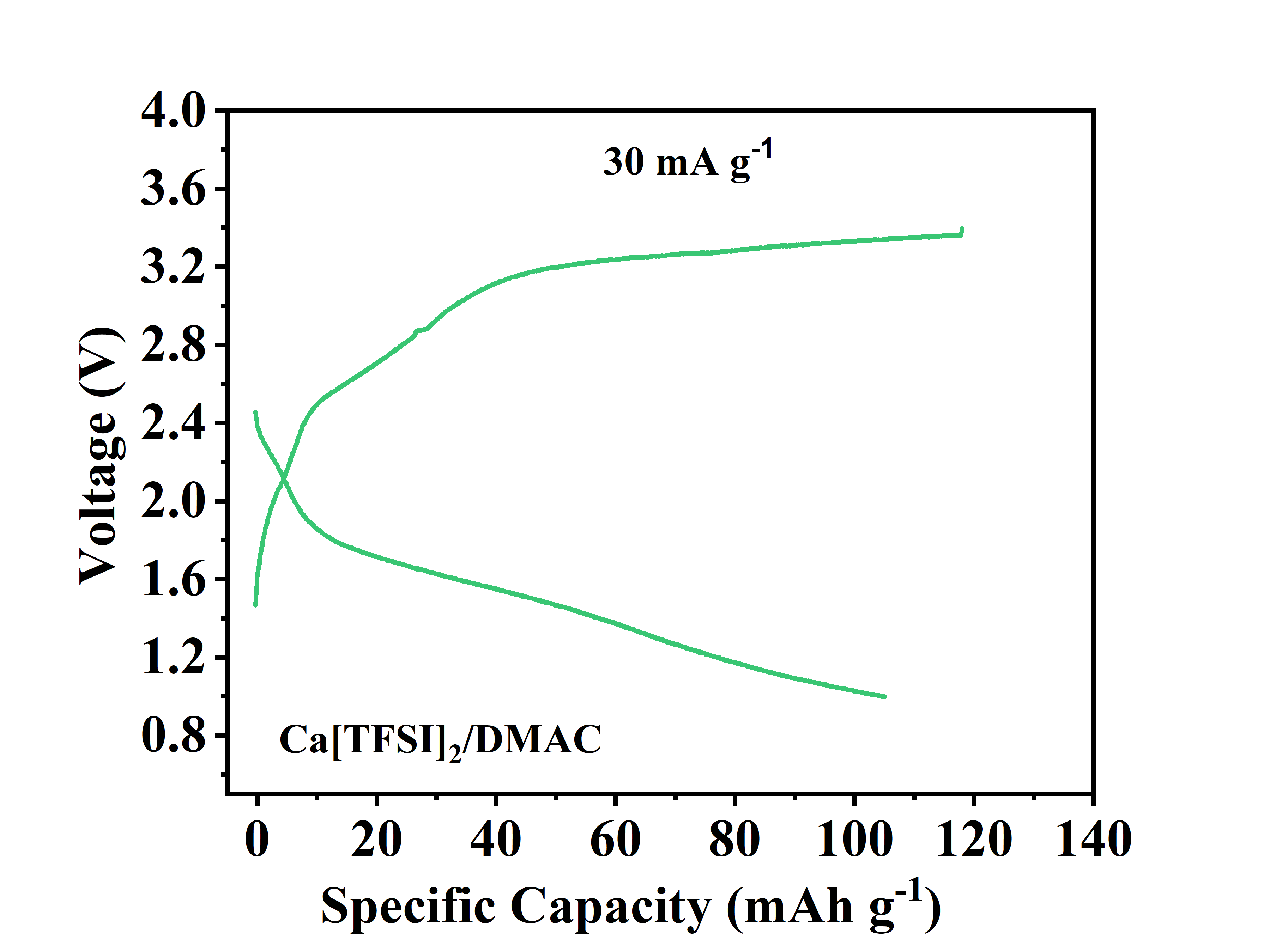
To explore the potential limitations or trade-offs of Mo doping, we tested the long-term stability of MMO-40 under practical conditions, such as high loading, low electrolyte volume, and high current density. First, we increased the cathode material loading from 1.5 mg cm⁻² to 4 mg cm⁻² (**Figure S12**), reduced the electrolyte volume from 80 μL to 40 μL, and applied a current density of 1000 mA g⁻¹ (which is currently a relatively high current density reported for calcium-ion battery cathode materials (**Table S3**)). As shown in the **Figure S13**, MMO-40 exhibits good specific capacity (63 mAh/g) and cycling performance (capacity retention of 78% after 1000 cycles). These results indicate that the introduction of Mo effectively enhances the material's conductivity and structural stability, significantly improving its long-term cycling performance under high current density and low electrolyte conditions.



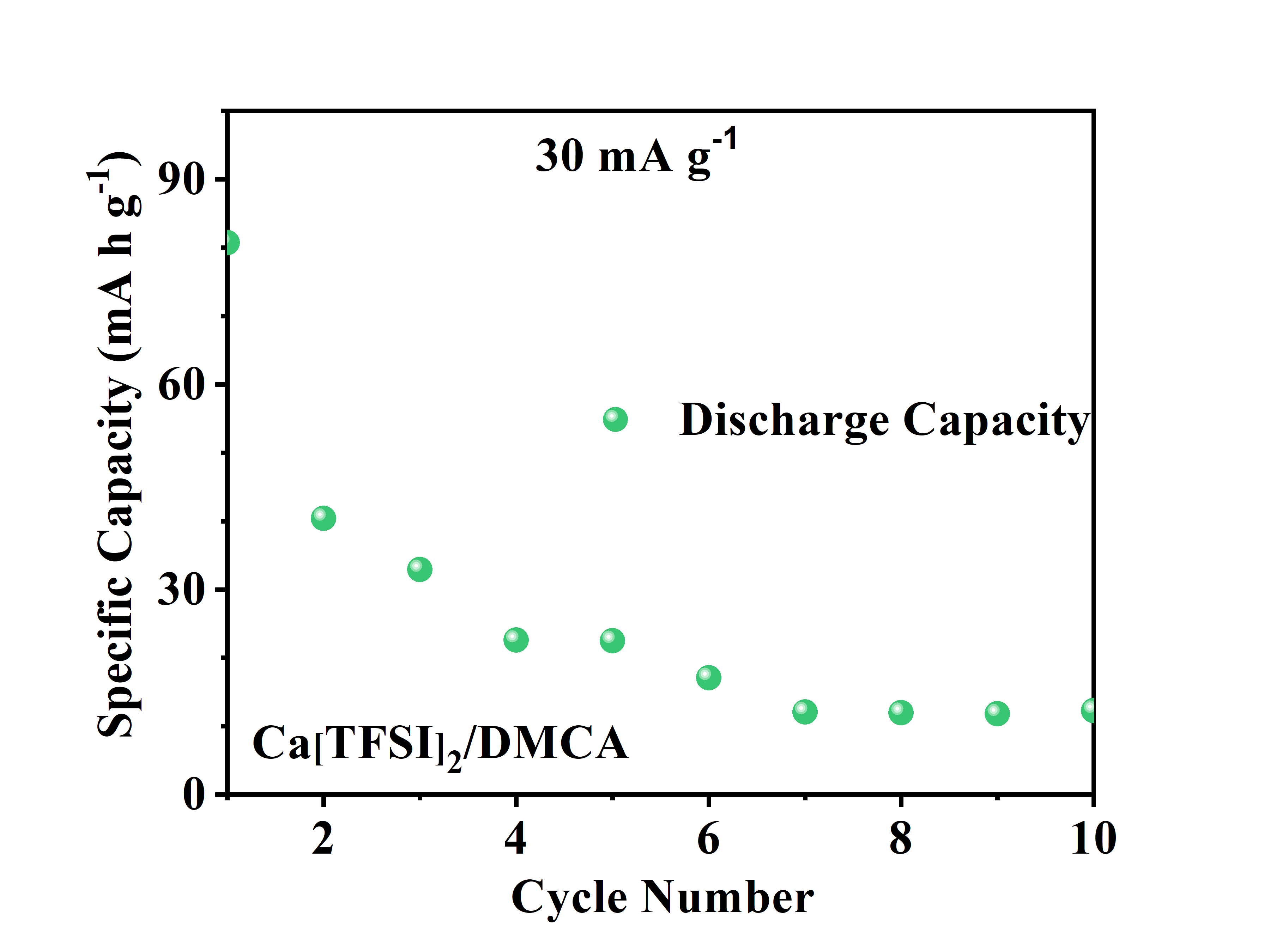
**Figure S12**. (a) The long side of the MMO-40 cathode material; (b) The short side of the MMO-40 cathode material



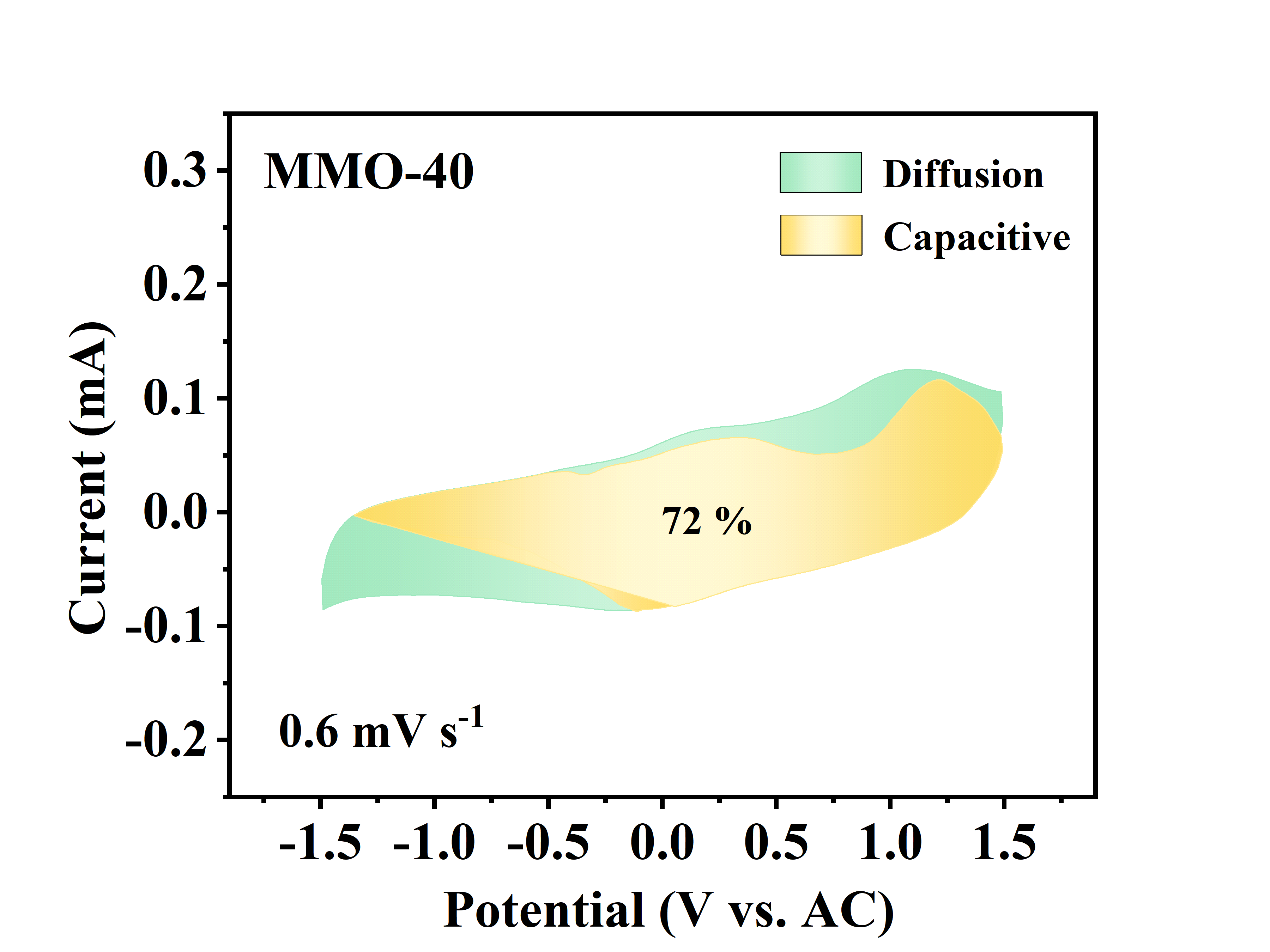
**Figure S13**. Cycling performance of MMO-40 at 1.0 A g−1.

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**Figure S14.** The charge/discharge curves of MMO-40 with Ca(TFSI)2/DMCA electrolyte at 30 mA g−1.

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**Figure S15.** The cycling performance of MMO-40 with Ca(TFSI)2/DMCA electrolyte at 30 mA g−1.



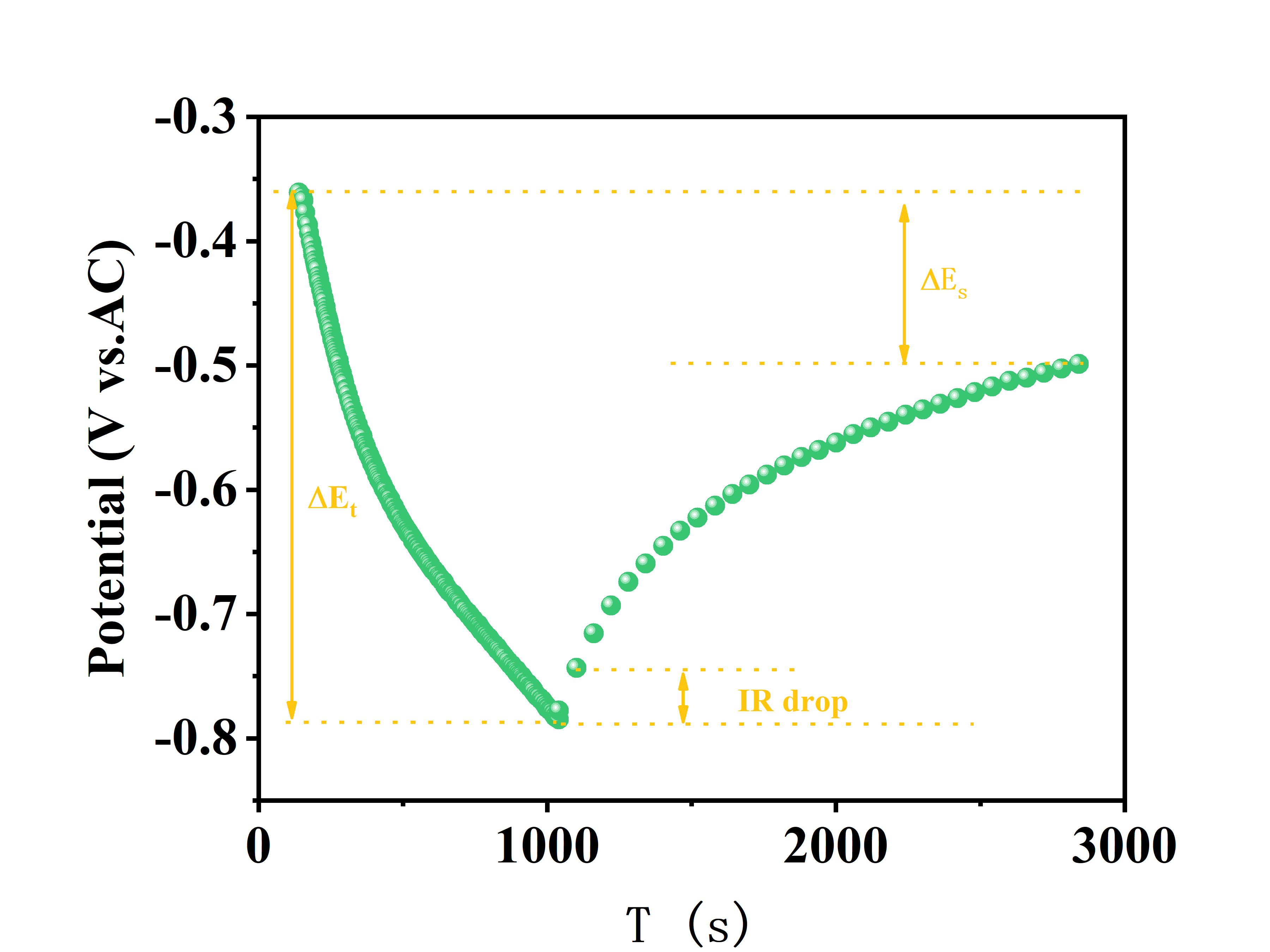
**Figure S16.** The calculated capacitive contribution to the charge storage of MMO-40 at 0.6 mV s−1.

**GITT test.**

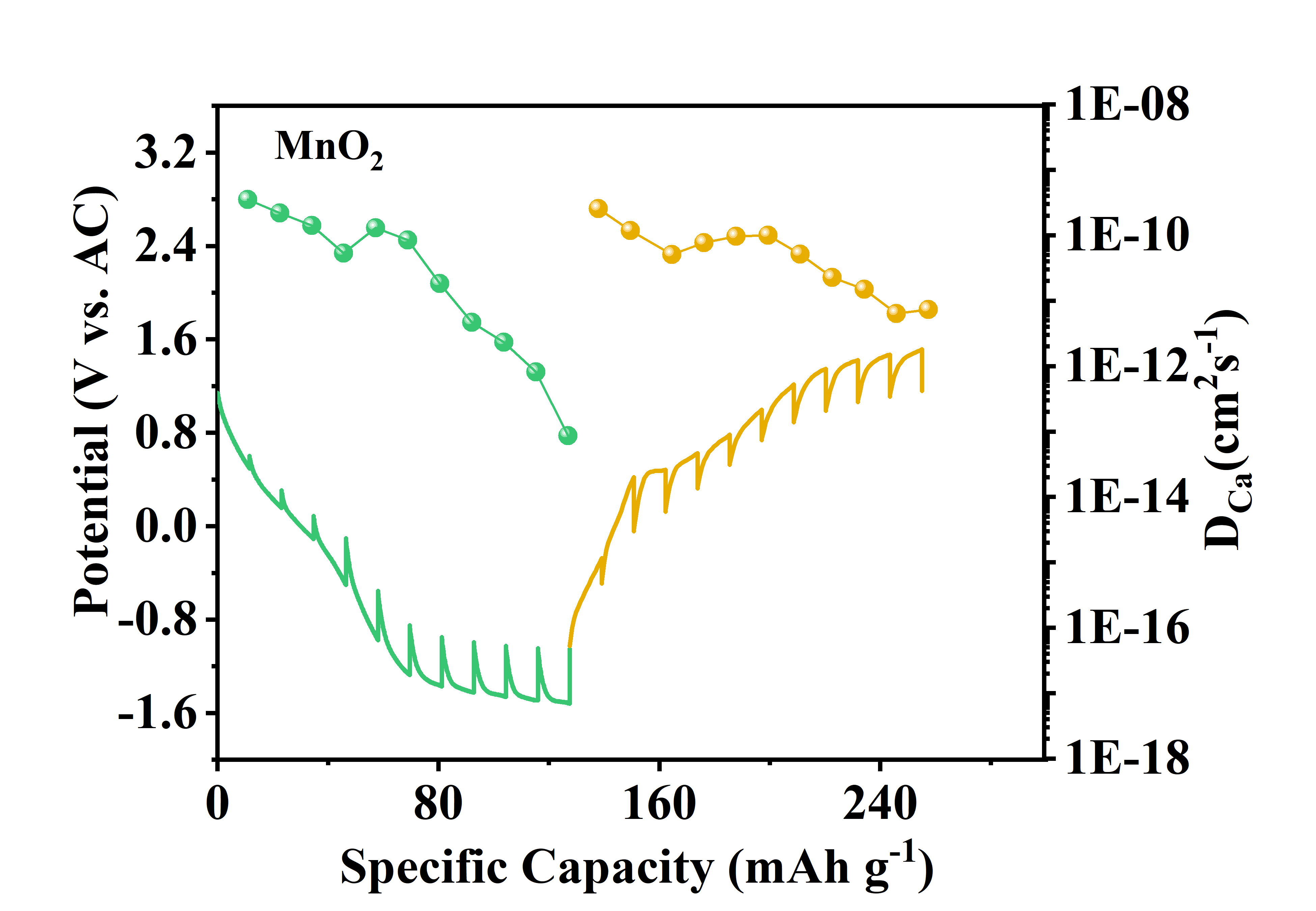
The dynamics of Ca ion solid-state diffusion in MMO-40 cathode was evaluated by employing galvanostatic intermittent titration technique (GITT). The Ca2+ ion diffusion diffusivity (DGITT) was obtained via the following equation:

(1)

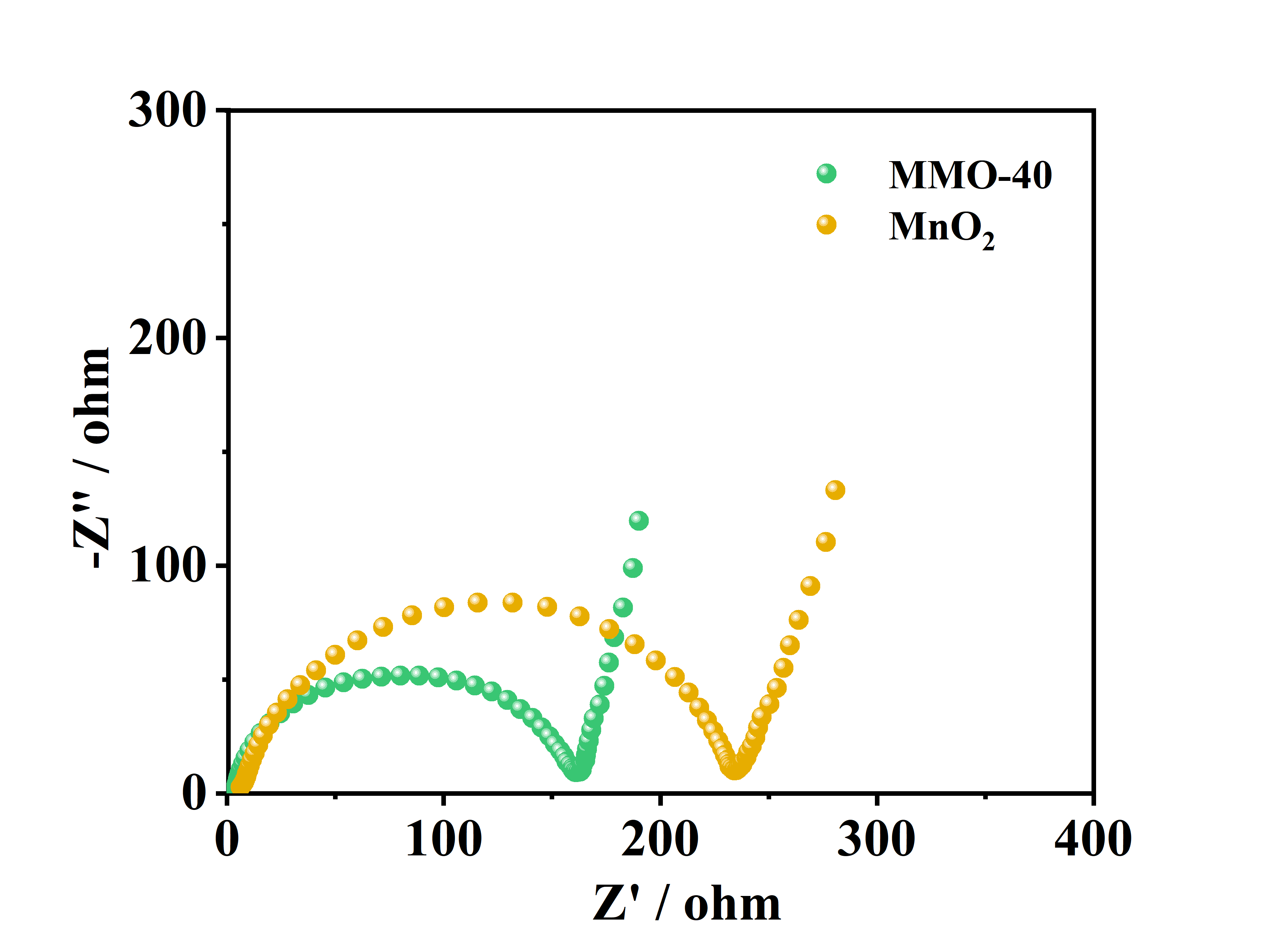
Where τ , mB, VM, and MB are the constant current pulse duration, the mass loading, the molar volume, and the molar mass of the intercalated electrode material, respectively. S is the interface area between electrode and electrolyte. After a current pulse is conducted in a single step GITT experiment, ΔES and ΔEτ represent the changes in steady-state voltage and total cell voltage regardless of the IR-drop, respectively. ΔEs and ΔEτ can be obtained from the GITT curves (**Figure S17**).



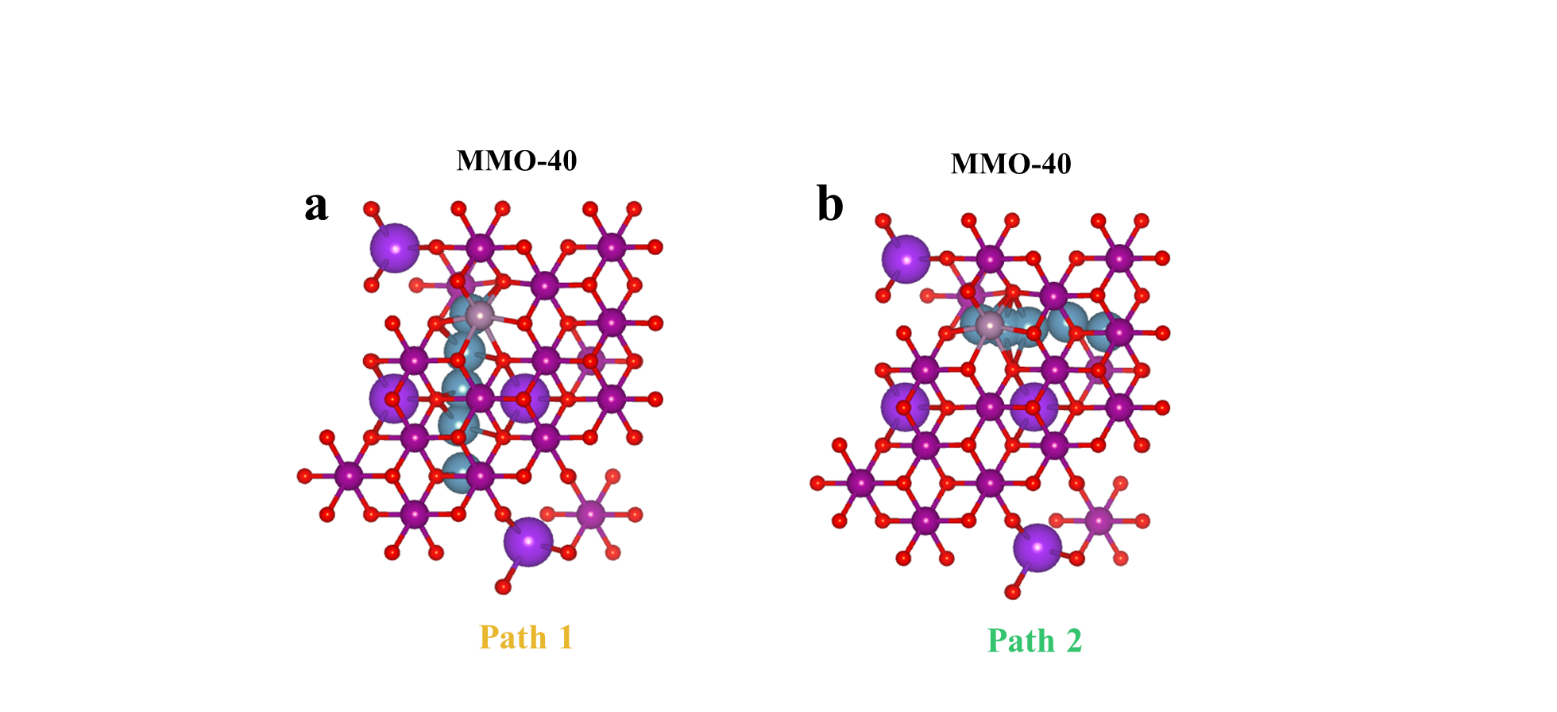
**Figure S17.** The potential-time curve in one pluse period of GITT test.

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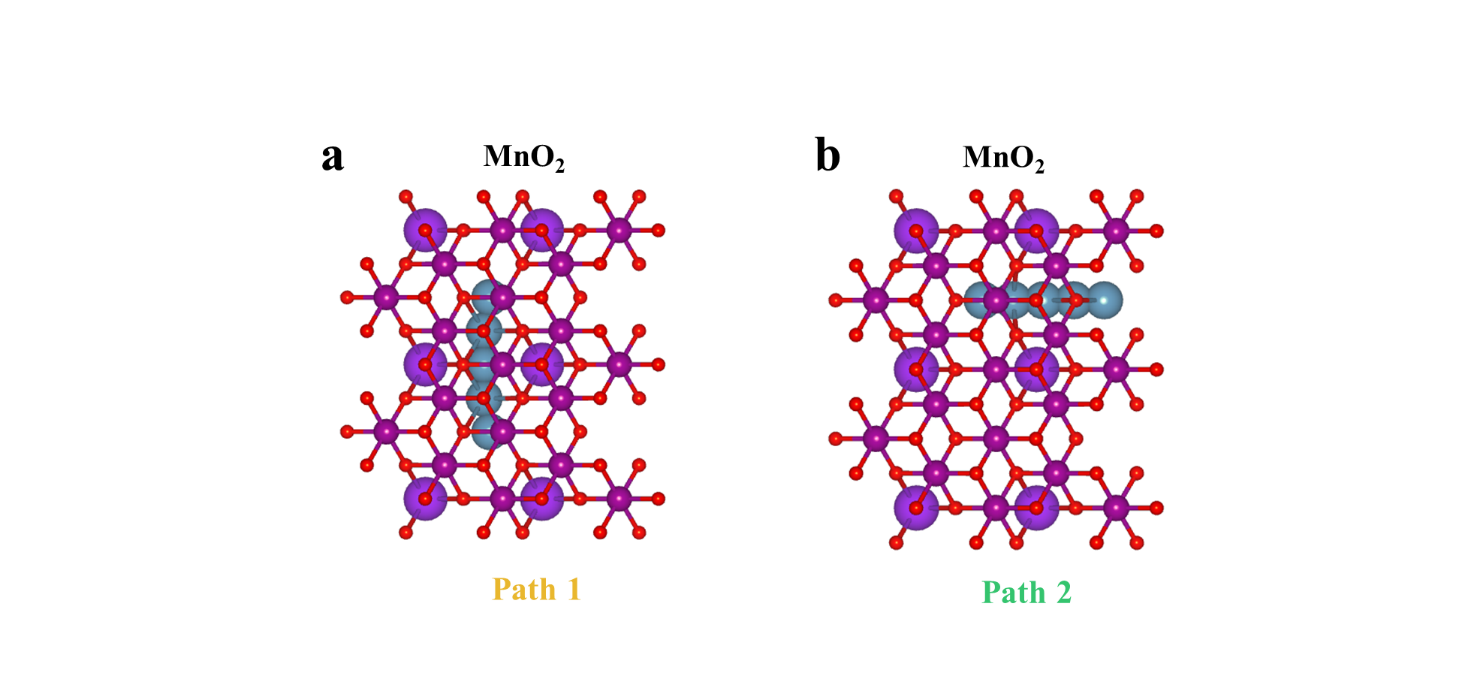
**Figure S18.** GITT profiles and the corresponding Ca2+ diffusion coefficients of MnO2 cathode.



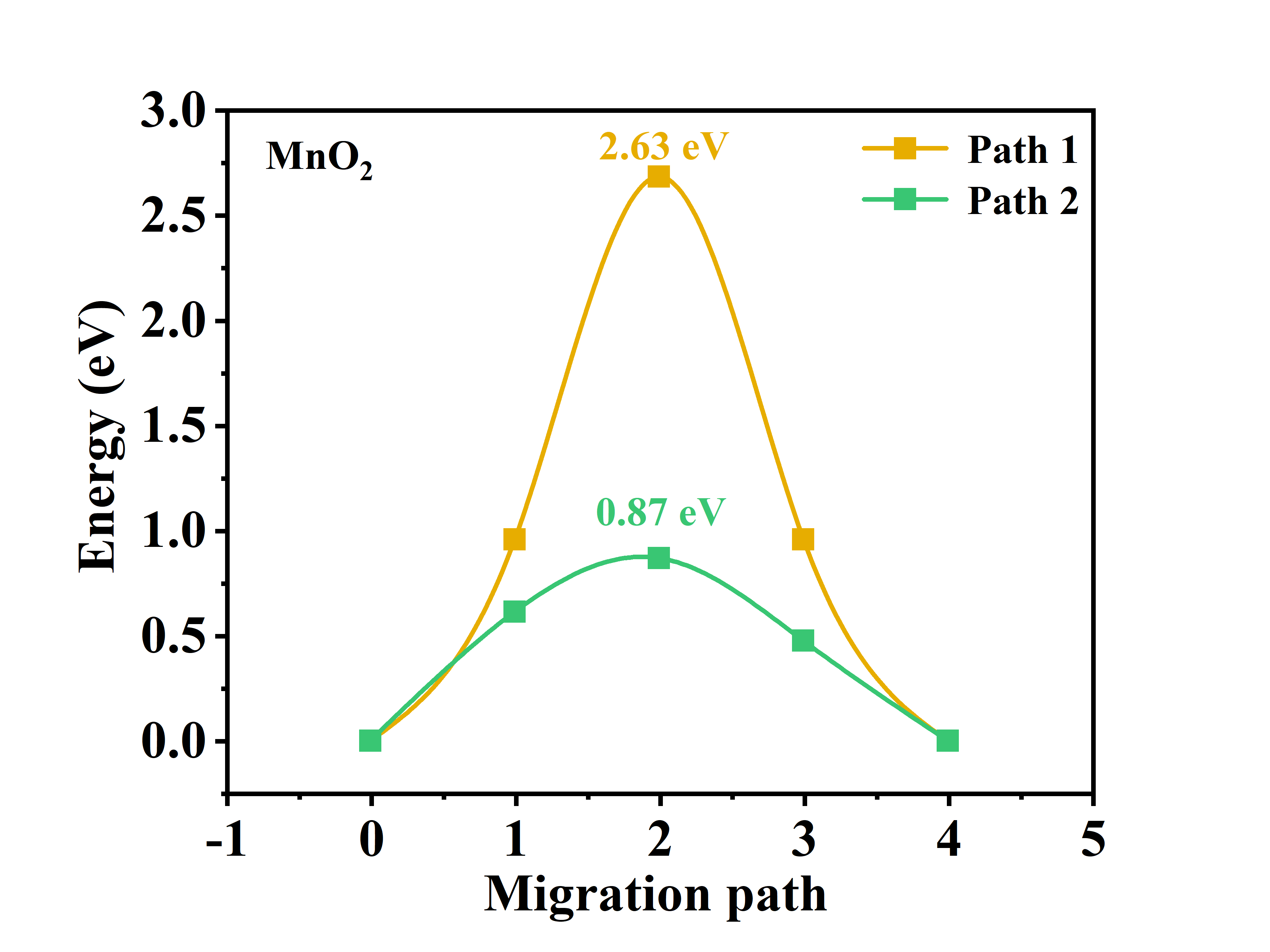
**Figure S19**. The EIS polts of the MMO-40 and MnO2.



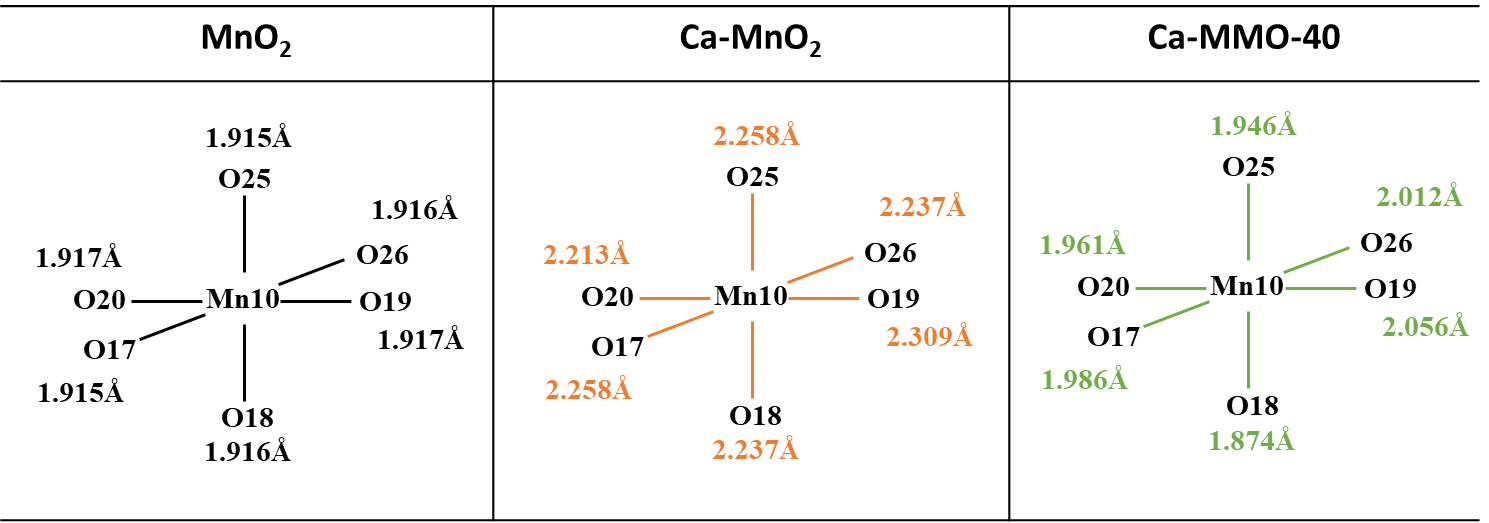
**Figure S20**. The diffusion path profiles of MMO-40 along (a) path 1 (b directions) (b) path 2 (a directions).



**Figure S21**. The diffusion path profiles of MnO2 along (a) path 1 (b directions) (b) path 2 (a directions).



**Figure S23**. Ca ions migration behaviors along the a, b-axis in MnO2.

**Table S4.** The Jahn-Teller distortion of Mn-O octahedral in different MnO2. ****

**Table S5.** The ICP results of MMO-40 electrodes at different states.

|  |  |  |  |
| --- | --- | --- | --- |
| **Materials** | **Ca** | **Mn** | **Ca/Mn** |
| **Pristine** | **0.01** | **0.44** | **0.02** |
| **1st discharge** | **0.04** | **0.45** | **0.10** |
| **1st charge** | **0.02** | **0.53** | **0.03** |
| **2nd discharge** | **0.04** | **0.41** | **0.11** |

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