Li$_{1.5}$La$_{1.5}$MO$_6$ ($M = W^{6+}, Te^{6+}$) as a new series of lithium-rich double perovskites for all-solid-state lithium-ion batteries

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Solid-state batteries are a proposed route to safely achieving high energy densities, yet this architecture faces challenges arising from interfacial issues between the electrode and solid electrolyte. Here we develop a novel family of double perovskites, Li$_{1.5}$La$_{1.5}$MO$_6$ ($M = W^{6+}, Te^{6+}$), where an uncommon lithium-ion distribution enables macroscopic ion diffusion and tailored design of the composition allows us to switch functionality to either a negative electrode or a solid electrolyte. Introduction of tungsten allows reversible lithium-ion intercalation below 1 V, enabling application as an anode (initial specific capacity >200 mAh g$^{-1}$ with remarkably low volume change of ~0.2%). By contrast, substitution of tungsten with tellurium induces redox stability, directing the functionality of the perovskite towards a solid-state electrolyte with electrochemical stability up to 5 V and a low activation energy barrier (<0.2 eV) for microscopic lithium-ion diffusion. Characterisation across multiple length- and time-scales allows interrogation of the structure-property relationships in these materials and preliminary examination of a solid-state cell employing both compositions suggests lattice-matching avenues show promise for all-solid-state batteries.
Accessing high performance all-solid-state Li-ion batteries remains an outstanding grand challenge in the battery research community. The desire to move towards an all-solid battery configuration is driven by safety concerns, enabling the use of metallic lithium anodes and the replacement of flammable liquid electrolytes used ubiquitously in existing Li-ion batteries. These liquid electrolytes are readily flammable and chemically unstable at high voltages and temperatures, which compromises the safety of the battery. All-solid-state Li batteries are a promising alternative, which could overcome not only these pressing safety concerns but would also see an increase in the achievable energy density in these Li batteries by extending the potential window to permit the safe use of high-voltage cathodes and metallic lithium anodes. However, a lack of reliable solid-state electrolytes is currently hampering the development of all-solid-state batteries and complexities of delivering high Li-ion diffusion at the electrode–electrolyte interface mean that there is a pressing need for new families of functional solid-state materials to fulfill this role.

To address this challenge, we have turned to the perovskite family of compounds, where the prototype cubic structure possesses the formula unit $\text{ABO}_3$, with A-site metal cations 12-coordinated to oxygen and B-site cations octahedrally coordinated by 6 oxygen atoms. Oxide perovskite materials are versatile materials with an impressive range of applications due to their exotic physical properties, including ferroelectric, dielectric, pyroelectric, and piezoelectric behaviours. This versatility owes much to the robust framework, which permits multiple combinations of different cations and anions to be present in the structure, making this an ideal candidate for battery applications as it can accommodate a wide range of cation sizes and oxidation states. Lower-symmetry structures can also be obtained by variations in the relative sizes of the $A$ and $B$ cations. Our intention is to derive a family of compounds where judicious choice of the B-site cation can lead to changes in conductivity, allowing for the design of active electrode and solid-electrolyte materials of the same structure type. Our ultimate ambition is to realise a family of lithium-containing materials where chemical compatibility and ion mobility at the electrode–electrolyte boundary are maximised by shared crystal structure and minimal changes in compositional variation across this interface.

Lithium is most commonly accommodated in the perovskite structure in the oxide octahedra. However, there is an extensively studied class of compounds where lithium is introduced into the larger site to give stoichiometries such as $\text{(La,Li)}\text{TiO}_3$. These materials continue to attract great interest owing to reports of fast ion conduction, e.g., $\text{Li}_{0.34}\text{La}_{0.5}\text{TiO}_2$ has not been reproduced in analogues based on replacement of $\text{La}^{3+}$ with other rare earth cations or alkaline earth elements or by substitution of $\text{Ti}^{4+}$ with $\text{Zr}^{4+}$, $\text{Nb}^{5+}$, $\text{Ta}^{5+}$ or other appropriate cations. Despite the multiple applications of perovskite materials, their use in Li-ion batteries is limited to only a few reports, namely, lithium lanthanum titanate as a fast lithium conductor and lithium lanthanum niobate as an insertion electrode. Introduction of a second cation on the $B$ site can introduce additional complexity from chemical ordering of these cations over different crystallographic sites in so-called double perovskite structures as shown in Fig. 1. We have serendipitously discovered a lithium tungstate double perovskite, which has also been independently identified by another group.

**Results**

**Synthesis, structural characterisation and chemical composition.** The syntheses of novel lithium-rich double perovskites $\text{Li}_x\text{La}_{1.5}\text{MO}_6$ ($\text{M} = \text{W}^{6+}$, $\text{Te}^{6+}$) used a microwave-assisted solid-state approach. Such synthetic methods have been developed extensively in our research group in recent years and afford faster, lower temperature routes to high quality solid-state...
Optimisation of the reagent stoichiometries revealed that ratios of Li:La:M of 1.5:1.5:1 were required for phase pure compounds (M = W\textsuperscript{6+}, Te\textsuperscript{4+}). Ratios lying outside of these values consistently delivered impure products as shown by X-ray diffraction (XRD) data in Supplementary Fig. 1. Diffraction data from three target compositions Li\textsubscript{1.5}La\textsubscript{1.5}WO\textsubscript{6}, Li\textsubscript{1.5}La\textsubscript{1.5}TeO\textsubscript{6} and Li\textsubscript{1.5}La\textsubscript{1.5}W\textsubscript{0.5}Te\textsubscript{0.5}O\textsubscript{6} could readily be indexed using a monochi-clinotically distorted variant of the perovskite structure. This distortion commonly arises from a combination of cation ordering over the octahedral sites and a tilting of the oxide octahedral to reduce the size of the large A-site interstice to better match the bonding requirements of A cations that are smaller than optimal. Li\textsuperscript{+} cations are well matched in size to the B-site octahedral sites as shown in the double perovskites La\textsubscript{1.5}Li\textsubscript{0.5}MIO\textsubscript{6} to emphasise the relation to the classic ABO\textsubscript{3} perovskite formula. This description implies that Li\textsuperscript{+} cations occupy both A and B sites of the structure, and this hypothesis was tested experimentally with X-ray and neutron powder diffraction (NPD). Using these two radiations in a simultaneous refinement allows the X-ray data to locate dominant X-ray scatterers, i.e. D\textsubscript{Li}, W\textsuperscript{6+} and Te\textsuperscript{4+}, and the neutron diffraction locates the lighter Li\textsuperscript{+} and O\textsuperscript{2—}. Crucially, the complementary weightings of atomic number (X-rays) and scattering length (neutrons) provides contrast that allows us to search for vacancies in these structures.

Rietveld refinement for La\textsubscript{1.5}Li\textsubscript{1.5}WO\textsubscript{6} showed that the A site is ca. 3/4 occupied by La\textsuperscript{3+}. The monoclinic distortion reduces the La coordination number to 8, from 12 in the undistorted structure. The A site is also partially occupied in a disordered manner by Li\textsuperscript{+} ions that are displaced towards the base of a trigonal pyramid (Fig. 1). This lowers the coordination number from eight for La\textsuperscript{3+} to four for Li\textsuperscript{+}, and the shortening of the Li–O distances to values more typical of the smaller Li\textsuperscript{+} cation. Trial refinements indicated that all oxide positions were within one esd, i.e. 1% of being fully occupied so these were subsequently fixed at this value. All other atomic fraction parameters and thermal parameters were allowed to refine freely leading to the stoichiometry La\textsubscript{1.43(12)}Li\textsubscript{1.39(4)}W\textsubscript{0.97(1)}O\textsubscript{6} (Supplementary Table 1), within three esd of the target stoichiometry. Elemental analyses by energy-dispersive analysis of X-rays and mass spectrometry were both in agreement with this (Supplementary Tables 2 and 3). The composition of this material will be assessed by X-ray absorption spectroscopy (XAS) using the EDX and ICP elemental analyses (Supplementary Tables 2 and 3). We recently reported the Na-analogue Na\textsubscript{1.5}La\textsubscript{1.5}TeO\textsubscript{6} indicating of the wide versatility of these novel families of alkali metal-rich double perovskites. The microstructures of Li\textsubscript{1.5}La\textsubscript{1.5}WO\textsubscript{6} and Li\textsubscript{1.5}La\textsubscript{1.5}TeO\textsubscript{6} feature quasi-spherical particles fused together by tubular joints as shown in Fig. 2. A larger particle size was noted for the tungsten compound (5–10 \(\mu\)m) compared with the tellurium analogue (1–5 \(\mu\)m).

Electrochemical and ion transport properties. The presence of W\textsuperscript{6+} ions and the robust perovskite framework suggest this material may function as an insertion anode material, due to the accessible tungsten redox couples. To evaluate this possibility, cyclic voltammetry (CV) analyses were performed in the voltage range of 0.01–2.8 V against Li metal as the counter electrode, at a scan rate of 0.1 mV s\textsuperscript{−1}. In the first cycle, a broad peak in the reduction regime is observed due to the formation of a solid-electrolyte interphase (SEI), a consequence of a partial decomposition at low voltages of the carbonate liquid electrolyte and the high surface area of the carbon black used\textsuperscript{26,27}. Li\textsubscript{1.5}La\textsubscript{1.5}WO\textsubscript{6} displays two strong redox couples (Fig. 3a). The first voltage redox couple occurs at ~0.7 V in the reduction regime and at ~1 V in the oxidation regime. The second redox process takes place at lower potentials; in the reduction regime the peak below 0.2 V is partially obscured by the broad peak near 0 V arising from lithium insertion into the carbon black additive\textsuperscript{27}, and near 0.3 V for the oxidation process. Interestingly, in the case of the isostructural Li\textsubscript{1.5}La\textsubscript{1.5}TeO\textsubscript{6} analogue, there are no reduction or oxidation peaks over the same potential range (Fig. 3b), apart from those arising from the carbon black additive (Supplementary Fig. 6). The intermediate phase Li\textsubscript{1.5}La\textsubscript{1.5}W\textsubscript{0.5}Te\textsubscript{0.5}O\textsubscript{6} (Supplementary Fig. 7) displays similar peak positions to the W parent compound, but with reduced current presumably from lower concentration of redox active W cations.

The absence of redox activity in Li\textsubscript{1.5}La\textsubscript{1.5}TeO\textsubscript{6} indicated that this compound could be redox stable in the potential window of a battery and suggested applications as a solid Li-ion electrolyte. Macroscopicionic conduction was analysed for both materials by means of electrochemical impedance spectroscopy (Fig. 4), revealing activation energies for ionic conduction of 0.59(3) and 0.68(2) eV (Fig. 5) and ionic conductivities of 1.1 × 10\textsuperscript{−5} and 5.8 × 10\textsuperscript{−3} S cm\textsuperscript{−1} at 124 °C for the W and Te materials, respectively (Supplementary Table 5). These conductivities are intermediate between the fast conducting garnets\textsuperscript{28–31} based on
Li$_7$La$_3$Zr$_2$O$_{12}$ and the lower conductivity of conventional garnets$^{32,33}$, such as the Li$_3$Ln$_3$Te$_2$O$_{12}$, that have the same cation ratio as these perovskites. It should be noted that these conductivities derive from sintered cold pressed pellets and include contributions from both intra- and inter-grain conduction. It is widely observed across garnets and other families of ionically conducting oxides that compositional adjustments may dramatically increase intra-grain conduction, whilst inter-grain resistance may be greatly reduced by systematic adjustments to processing conditions, e.g., hot pressing or spark-plasma sintering (SPS)$^{34,35}$. The Li-rich family of materials presented here are prime candidates for similar developments, with the added

![Figure 2](image1.png)

**Fig. 2 Crystal structure Rietveld refinements and particle morphology.** a X-ray and b neutron powder diffraction data for the Li$_{1.5}$La$_{1.5}$WO$_{6}$ material shown in the inset to (a). b Neutron diffraction data are shown over the combined Q-range 1–13 Å$^{-1}$ using two detector banks. c, d Corresponding data from Li$_{1.5}$La$_{1.5}$TeO$_{6}$. Fits were in good agreement to the monoclinic space group P$2_1/n$, with a partially disordered arrangement of oxide anions in Li$_{1.5}$La$_{1.5}$TeO$_{6}$. The SEM images reveal smaller particle sizes for the Te compound compared to the W analogue.

![Figure 3](image2.png)

**Fig. 3 Redox response dependence of M$^{6+}$cation.** a CV data for Li$_{1.5}$La$_{1.5}$WO$_{6}$ and b Li$_{1.5}$La$_{1.5}$TeO$_{6}$ materials mixed with 5% carbon black and 5% PTFE binder between 0.01 and 2.8 V vs Li. The scan rate was fixed at 0.1 mV s$^{-1}$ for both measurements.

Li$_7$La$_3$Zr$_2$O$_{12}$ and the lower conductivity of conventional garnets$^{32,33}$, such as the Li$_3$Ln$_3$Te$_2$O$_{12}$, that have the same cation ratio as these perovskites. It should be noted that these conductivities derive from sintered cold pressed pellets and include contributions from both intra- and inter-grain conduction. It is widely observed across garnets and other families of ionically conducting oxides that compositional adjustments may dramatically increase intra-grain conduction, whilst inter-grain resistance may be greatly reduced by systematic adjustments to processing conditions, e.g., hot pressing or spark-plasma sintering (SPS)$^{34,35}$. The Li-rich family of materials presented here are prime candidates for similar developments, with the added
The total conductivity measured by impedance spectroscopy can be complemented by muon spin relaxation (μ+SR) in assessing diffusion behaviour over a local scale of a few nanometres. Spin-polarised muons are implanted into the material and the spin direction is perturbed by the passage of diffusing species, such as Li⁺, that possess a nuclear moment. Analysis of the muon depolarisation as a function of temperature, combined with knowledge of the crystallographic distribution of Li⁺, allows extraction of values of room temperature Li⁺ diffusion coefficients of $6.6 \times 10^{-12}$ cm² s⁻¹ and $1.8 \times 10^{-11}$ cm² s⁻¹ for the W and Te materials, respectively, as shown in Figs. 4 and Supplementary Fig. 8. These values are similar to those obtained for other fast ion conductors studied using μ+SR, including the doped garnet materials based on Li₁₋ₓLaₓZr₂O₇ (4.62 $\times$ 10⁻¹¹ cm² s⁻¹), the anode material Li₄Ti₅O₁₂ (3.2 $\times$ 10⁻¹¹ cm² s⁻¹) and the high energy NMC cathode (3.5 $\times$ 10⁻¹² cm² s⁻¹)²¹,³⁸,³⁹. Arrhenius analyses, shown in Fig. 5, deliver activation energies of 0.136(5) for the W compound and 0.196(8) eV for the Te analogue. These values are also similar to those obtained for Na⁺ diffusion in our recently reported analogous Na-rich double perovskite, Na₁₋ₓLaₓTeO₆, of 4.2 $\times$ 10⁻¹² cm² s⁻¹ and 0.163(9) eV²³, indicating the versatility of the double perovskite framework for other battery chemistries beyond lithium. Our values from μ+SR experiments are in agreement with DFT calculations and NMR measurements previously reported on the tungstate¹⁹ and are also in line with those of the related (Li,La)TiO₃ perovskite fast ionic conductors materials (0.144 eV)¹³. These activation energies are much lower than we observe by total electrical impedance measurements for Li₁₋ₓLaₓWO₆ and Li₁₋ₓLaₓTeO₆. An individual muon samples a small, local region of a material and by implanting muons
Throughout the material samples a volume-weighted average structure. As grain boundaries make up a minority of the volume of crystalline materials, such as these perovskites, the transport properties derived from muon measurements are strongly weighted towards the intra-grain transport properties. We have seen similar effects in fast Li\textsuperscript{+} conducting garnet phases where the muon activation energy is much lower than that derived from impedance analysis of total conductivity\textsuperscript{21}.

\textit{Li\textsubscript{1.5}La\textsubscript{1.5}WO\textsubscript{6}} shows ionic conductivity and low-voltage redox activity, suggesting possible application as an anode in Li-ion batteries. As CV measurements on \textit{Li\textsubscript{1.5}La\textsubscript{1.5}TeO\textsubscript{6}} showed no redox activity, galvanostatic measurements on the Te analogue were carried out in order to serve as null measurements and evaluate the capacitive contribution from the carbon black additive used to increase the electronic conductivity of the electrode.

Galvanostatic testing of \textit{Li\textsubscript{1.5}La\textsubscript{1.5}WO\textsubscript{6}} at a rate of 36 mAh g\textsuperscript{−1} gave the cycling profile and discharge capacity shown in Fig. 6. The first discharge capacity is irreversibly increased to above 300 mAh g\textsuperscript{−1} due to electrolyte decomposition and formation of SEI. Subsequent cycles displayed reversible capacities of \approx 125 mAh g\textsuperscript{−1} corresponding to an approximate 2e\textsuperscript{−} transfer per formula unit of double perovskite material after carbon capacity subtraction determined from the \textit{Li\textsubscript{1.5}La\textsubscript{1.5}TeO\textsubscript{6}} cycling capacity. In agreement with the CV results, a clear flat plateau is observed for \textit{Li\textsubscript{1.5}La\textsubscript{1.5}WO\textsubscript{6}} at 0.35 V and the onset of a pseudo-plateau at \approx 0.7 V during charging. On the discharging cycles, a pseudo-plateau is observed below 0.9 V and a plateau at \approx 0.2 V. The mixed metal \textit{Li\textsubscript{1.5}La\textsubscript{1.5}WO\textsubscript{6}Te\textsubscript{0.3}O\textsubscript{6}} compound was found to have a discharge capacity intermediate between the parent \textit{Li\textsubscript{1.5}La\textsubscript{1.5}MO\textsubscript{6}} compounds, confirming the redox activity experienced in these double perovskites is due to the W\textsuperscript{6+} cations. Carbon coating of the \textit{Li\textsubscript{1.5}La\textsubscript{1.5}WO\textsubscript{6}} particle surface was performed via a sucrose impregnation-carbonisation route in order to improve the performance and cyclability of the \textit{Li\textsubscript{1.5}La\textsubscript{1.5}WO\textsubscript{6}} anode material. Carbon coating improves the electronic properties of the electrode composite and can also act as a buffer layer to protect from continuous side-reactions between the active materials surfaces and the electrolyte. The carbon-coating treatment resulted in an increased discharge capacity (Supplementary Fig. 9) with a value above 200 mAh g\textsuperscript{−1} up to cycle 15, doubling that of the uncoated material’s capacity of \approx 100 mAh g\textsuperscript{−1}. Retention capacity is also greatly improved with the carbon-coating approach, with an increase from 53 to 85% on cycle 15 and from 41 to 62% at the end of cycle 20.

Assessing the redox activity of the tungsten analogue presented a challenge. XAS measurements of W L\textsubscript{III}-edge (Supplementary Fig. 10) were performed on ex situ cycled samples but assigning oxidation state changes are difficult due to overlapping absorption edges. Only small differences in the relative intensity of the L\textsubscript{III} split peak were observable making it difficult to attribute these directly to oxidation changes of W. difficulties in the analysis of W oxidation states by XAS has been previously reported in the literature\textsuperscript{41}. Instead, we have used magnetometry to follow the reduction from diamagnetic W\textsuperscript{6+} (5d\textsuperscript{0}) to paramagnetic species W\textsuperscript{5+} or W\textsuperscript{4+} during cycling. Measurements were conducted on two samples; a fully discharged sample and a sample charged back to 0.4 V (just above the first oxidation process). Magnetic measurements on the cycled materials point to oxidation state changes on the tungsten ions (Supplementary Fig. 11). For materials discharged to 0.01 V, Curie–Weiss paramagnetism indicative of fully localised unpaired electrons is observed arising from 1.43 \mu\textsubscript{B} per formula unit, corresponding to the formation of 0.8 mol of W\textsuperscript{5+} per formula unit. The observed Weiss constant of \approx −120(2) K indicates strong antiferromagnetic coupling between neighbouring magnetic centres. In conjunction with the observed moment this shows that around 0.8 W\textsuperscript{5+} cations per formula unit are interacting strongly, indicating short superexchange distance between these paramagnetic cations. This implies the W\textsuperscript{5+} are evenly distributed throughout the perovskite phase that has a composition of \textit{Li\textsubscript{1.5}La\textsubscript{1.5}WO\textsubscript{6}}. From galvanostatic measurements, we expect to observe W\textsuperscript{4+} at this voltage, suggesting that not all of the observed reduction leads to formation of localised, unpaired electrons. Instead, the excess 1.2 electrons per formula unit must lead to species that make no significant contribution to the Curie–Weiss behaviour. Delocalisation of some electrons leading to Pauli paramagnetism or a conversion reaction to a diamagnetic species would both be magnetically undetectable in the presence of the dominant signal from the W\textsuperscript{5+}. Cycling the material back to 0.4 V, beyond the first oxidation process, revealed a change in the magnetism of the cycled material with a large reduction of the paramagnetic moment to 0.84(3) \mu\textsubscript{B} and a weak positive Curie constant of \theta = +9(1) K. This indicates almost complete re-oxidation to W\textsuperscript{6+}.

Ex situ PXRD of fully discharged material revealed that the perovskite structure of \textit{Li\textsubscript{1.5}La\textsubscript{1.5}WO\textsubscript{6}} is retained upon lithiation with a small displacement of the diffraction peaks towards higher d-spacing values, which is then reversed when the material is charged back to 2.8 V (Fig. 7). The absence of other phases in these diffraction patterns suggests intercalation as the main

\textbf{Fig. 6 Battery cycling behaviour of \textit{Li\textsubscript{1.5}La\textsubscript{1.5}MO\textsubscript{6}} Li-rich double perovskites. a} Galvanostatic cycling of \textit{Li\textsubscript{1.5}La\textsubscript{1.5}MO\textsubscript{6}} double perovskites mixed with 5% carbon black and 5% PTFE binder, between 0.01 and 2.8 V vs Li at a specific current of 36 mA g\textsuperscript{−1}, where the first discharge has been omitted for clarity. \textit{b} Charge/discharge capacity fading test for the \textit{Li\textsubscript{1.5}La\textsubscript{1.5}WO\textsubscript{6}} material mixed with 5% carbon black and 5% PTFE binder at a current of 36 mA g\textsuperscript{−1} between 0.01 and 2.8 V vs Li over 20 cycles. The initial high first discharge is due to the irreversible formation of the SEI layer caused by electrolyte decomposition.
mechanism for the observed electrochemical activity of this material. Interestingly, the small lattice parameter change indicates only a small volume increase from 245.016(3) Å before cycling to 245.50(2) Å post-lithiation. This 0.2% change is remarkably low compared to electrodes such as LiFe0.8Mn0.2SO4F, which shows a volume change of 0.6% between the lithiated and delithiated phases\textsuperscript{42,43}, or LiFePO\textsubscript{4} where larger volume changes of 6.6% are noted\textsuperscript{44}. The titanate anode material Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} also shows that reductive insertion of lithium is most readily achieved by incorporation of additional lithium into the large A site interstices that already contain Li\textsuperscript{+}, with displacement of the Li\textsuperscript{+} cations away from the centre of the hole to give lower coordination numbers and minimising the electrostatic repulsion arising from Li--Li interactions. The structure for Li\textsubscript{2.5}La\textsubscript{1.5}WO\textsubscript{6} contains three Li\textsuperscript{+} cations occupying a single A site forming tetrahedral LiO\textsubscript{4} units and maintaining a minimum Li--Li separation of at least 2.44 Å. This stoichiometry corresponds to reduction to W\textsuperscript{5+} and is in agreement with that indicated by the magnetometry measurements. Simulations can push the Li\textsuperscript{+} content towards a limit of Li\textsubscript{3.0}La\textsubscript{1.5}WO\textsubscript{6} giving four Li\textsuperscript{+} cations in the A site. This configuration involves somewhat shorter Li--Li distances, down to 2.29 Å, and considerable distortion of the LiO\textsubscript{6} and WO\textsubscript{6} units. Simulations on Li\textsubscript{1.5}La\textsubscript{1.5}TeO\textsubscript{6} show that, as expected, the 4d\textsuperscript{10} configuration of Te\textsuperscript{6+} presents a barrier to reductive intercalation. Interestingly, Bader charge analysis of the oxidation states of tungsten in the Li\textsubscript{1.5}La\textsubscript{1.5}WO\textsubscript{6} systems shows a defined stepwise change from Li\textsubscript{1.50}La\textsubscript{1.5}WO\textsubscript{6} (W\textsuperscript{6+}, d\textsuperscript{9}) to Li\textsubscript{2.50}La\textsubscript{1.5}WO\textsubscript{6} (W\textsuperscript{5+}, d\textsuperscript{10}) to Li\textsubscript{3.00}La\textsubscript{1.5}WO\textsubscript{6} (W\textsuperscript{4+} and W\textsuperscript{3+} in 50:50 ratio, suggesting mixed d\textsuperscript{1} and d\textsuperscript{2} configurations) (Supplementary Fig. 12). Above Li\textsubscript{3.00}La\textsubscript{1.5}WO\textsubscript{6} the structure becomes heavily distorted and the electronic structure no longer follows a simple trend. Analogous calculations on the Li\textsubscript{1.5}La\textsubscript{1.5}TeO\textsubscript{6} structure (Supplementary Fig. 13 and Supplementary Table 7) have revealed large intercalation voltages for Li\textsuperscript{+} intercalation together with reluctance of Te\textsuperscript{6+} to form Te\textsuperscript{5+}, suggesting redox cycling of the Te analogue to be unlikely, as experimentally observed. Density of state analysis (Supplementary Fig. 14) also confirms the stability of this material against oxidation, with a large band gap of ca. 5 eV in the case of the Li\textsubscript{1.5}La\textsubscript{1.5}TeO\textsubscript{6} material, indicating high electrochemical stability as solid-state electrolyte.

In order to account for the observed two-electron transfer during cycling, we must consider alternative processes that may contribute to this increased capacity, such as conversion reaction to Li\textsubscript{2}O\textsubscript{4}\textsuperscript{7}. From diffraction patterns of the cycled Li\textsubscript{1.5}La\textsubscript{1.5}WO\textsubscript{6} materials, there is no evidence of crystalline conversion products and scanning electron microscopy (SEM) images of post-cycled material do not suggest significant degradation of the electrode (Supplementary Fig. 15). To shed more light onto the possible

**Fig. 7** Li\textsubscript{1.5}La\textsubscript{1.5}WO\textsubscript{6} crystal lattice evolution upon cycling. a Ex situ XRD patterns of the Li\textsubscript{1.5}La\textsubscript{1.5}WO\textsubscript{6} material as-synthesised, after fully electrochemical lithiation and after subsequent de-lithiation (20 cycles) (green line). b Magnification of the (220) peak evidences the reversible insertion and de-insertion of Li ions to and from the structure. The calculated volume expansion upon full lithiation is 0.2%.
mechanism responsible for the additional capacity, we further examined the mixed metal Li$_{1.5}$La$_{1.5}$W$_{0.5}$Te$_{0.5}$O$_6$ phase. Interestingly, Li$_{1.5}$La$_{1.5}$W$_{0.5}$Te$_{0.5}$O$_6$ does not show a clear low redox couple in contrast to the well-defined peaks observed for Li$_{1.5}$La$_{1.5}$WO$_6$. Furthermore, this partial substitution of W$^{6+}$ by Te$^{6+}$ resulted in a reduction of the material specific capacity greater than that corresponding to decreasing concentration of redox active W$^{6+}$. Specifically, the observed capacity on the third cycle of ca. 120 mAh g$^{-1}$ in Li$_{1.5}$La$_{1.5}$WO$_6$ decreased to ca. 50 mAh g$^{-1}$ in Li$_{1.5}$La$_{1.5}$W$_{0.5}$Te$_{0.5}$O$_6$ and considering that the carbon black in the redox-inactive Li$_{1.5}$La$_{1.5}$TeO$_6$ provides near 25 mAh g$^{-1}$ (Fig. 6a), the reduction of the capacity when replacing half of W$^{6+}$ by Te$^{6+}$ in Li$_{1.5}$La$_{1.5}$W$_{0.5}$Te$_{0.5}$O$_6$ is almost fourfold (from ~95 to 25 mAh g$^{-1}$). In addition to this capacity loss, the long-range crystalline structure of Li$_{1.5}$La$_{1.5}$W$_{0.5}$Te$_{0.5}$O$_6$ is largely lost during the first battery discharge (Supplementary Fig. 16) suggesting a conversion-type process may be occurring for this material when reduced. The higher entropy of the resulting Li$_{1.5}$La$_{1.5}$W$_{0.5}$Te$_{0.5}$O$_6$ solid-solution phase could be the driving force underpinning the total macroscopic conversion, similarly reported for high entropy oxide materials in energy storage applications.$^{48,49}$

The CV data of the Li$_{1.5}$La$_{1.5}$TeO$_6$ parent compound also show a lower reversibility of the higher voltage redox couple (around 1 V), an observation more commonly found in conversion processes.$^{50-52}$ These observations, combined with the results of magnetic measurements and structural simulations, suggest that the low-voltage redox processes observed for the pure tungsten material are a result of intercalation, while the behaviour at higher voltages may involve conversion processes, reminiscent of previous reports for other W$^{6+}$ oxides.$^{53-56}$ Similar combined mechanisms have been observed in LiVO$_3$, which displays both intercalation and conversion behaviour below 2 V, involving formation of Li$_{2.5}$VO$_3$ and conversion into metallic vanadium and Li$_2$O.$^{57}$ Other bimetallic vanadates have been reported to undergo an initial conversion process within the particles’ surfaces followed by a intercalation process with subsequent Li$^+$ insertions.$^{58-60}$ Furthermore, unlike the Li$_{1.5}$La$_{1.5}$TeO$_6$ material, the Li$_{1.5}$La$_{1.5}$WO$_6$ material presents micromcron-sized particles on the bulk surface, which could be more prone to conversion reactions (Supplementary Fig. 17).

A key motivation for employing solid electrolytes in all-solid-state batteries is their potential to safely facilitate metallic lithium as an anode material.$^{61,64}$ To study the redox stability of Li$_{1.5}$La$_{1.5}$TeO$_6$ against lithium metal, an asymmetric cell was assembled using Li metal as a reference electrode and plasma deposited gold as a counter electrode. CV measurements at 80 °C reveal the ability of Li$_{1.5}$La$_{1.5}$TeO$_6$ to plate and strip lithium metal with no observable overpotential (Supplementary Fig. 18). Several peaks are observed in the reduction sweep of the first cycle, indicating the possible formation of an interfacial layer.$^{62}$ Subsequent cycles reveal that this interfacial layer bestows stability, with no further surface reactions noted. Interestingly, Li$_{1.5}$La$_{1.5}$TeO$_6$ displays good stability beyond 5 V making it a candidate for use in high-voltage cells. It should be noted that this is the first work on this novel material and that further optimisation, similar to that experienced by other solid-electrolyte systems (e.g., though microstructure optimisation for better Li wetting, protective layers to avoid reactions with electrodes)$^{63,64}$, is expected.

To optimise the ionic conductivity of the Li$_{1.5}$La$_{1.5}$TeO$_6$ material as a solid-state electrolyte, highly dense pellets were obtained by SPS. The relative density of the SPS pelletted material was greatly increased from ca. 76 to 98.1(1)%. Polarisation tests (Fig. 9a) indicate excellent compatibility and stability between Li metal and Li$_{1.5}$La$_{1.5}$TeO$_6$ during plating and stripping with Li electrodes. Impedance analysis of the Li$_{1.5}$La$_{1.5}$TeO$_6$ symmetric cells (Fig. 9b) reveals differences in the spectra observed for Li electrodes compared to Pt blocking electrodes. The latter contain a low frequency tail; this contrasts with the second semicircle observed when using Li electrodes, indicating the macroscopic mobility of Li$^+$. The small second semicircle observed when using Li electrodes is indicative of a low charge transfer resistance at the Li/Li$_{1.5}$La$_{1.5}$TeO$_6$ interface. Improvements in ionic conductivity are observed for the SPS treated Li$_{1.5}$La$_{1.5}$TeO$_6$ with a value of 0.12 mS cm$^{-1}$ at 124 °C, doubling that of the cold pressed material. The activation energy for Li$^+$ diffusion is also greatly reduced to 0.42(1) eV (Fig. 9b inset). This improvement in transport properties demonstrates the key role that pellet microstructure engineering has on the macroscopic conductivity measured by conventional electrochemical techniques, encouraging dedicated work to optimise this performance further. Subsequent improvement of conduction properties in novel oxide materials following their original report in the literature is often observed. For instance, benchmark Li-rich garnets oxides were originally reported to have ionic conductivities on the order of 10$^{-6}$ S cm$^{-1}$ with
densities were 50 and 100 μA cm−2 at 80 °C. The low local Li+ activation energy below 0.2 eV and similar Li+ diffusion coefficient obtained by μSR here for the Li1.5La1.5TeO6 material is comparable to that of the LLZO benchmark garnet electrolyte probed by the same technique, where again pellet microstructure greatly impacts the macroscopic transport properties\(^6\). This reinforces the scope for future improvements on the macroscopic transport properties of the Li1.5La1.5TeO6 double perovskite reported here.

To evaluate the efficacy of the approach of crystal structure matching across the electrode–electrolyte interface, we tested the compatibility of the Li1.5La1.5WO6 low-voltage negative electrode with the Li1.5La1.5TeO6 solid-state electrolyte in a quasi-solid-state battery. This was carried out using a Li-metal half-cell comprising by the Li1.5La1.5WO6 material as the electrode material and a hybrid electrolyte formulation Li1.5La1.5TeO6:LiTFSI:Py14TFSI (80:1:19%wt) [Py14TFSI = 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide] without the need for a separator or liquid electrolyte. The presence of the Py14TFSI ionic liquid affords better wettability between the electrode and solid-electrolyte phases as well as lowering the resistance of Li+ diffusion through the Li1.5La1.5TeO6 solid-electrolyte under the conditions employed. CV analyses at 80 °C (Fig. 10) reveal the clear redox response of Li1.5La1.5WO6, reminiscent of that observed for the conventional liquid electrolyte cell. The low-voltage reduction peak at ~0.63 V is most likely due to the irreversible formation of SEI at the carbon black surface from the Py14TFSI ionic liquid, in agreement with that also observed for the conventional liquid electrolyte cell. The low-voltage redox peaks appear more defined and sharper when the Li1.5La1.5TeO6 electrolyte is employed, indicating improved kinetics for Li+ transference and insertion. The additional irreversibility observed during the first cycle of the Li1.5La1.5TeO6 CV in the Li|Li1.5La1.5TeO6|Au cell (Supplementary Fig. 18) could be arising from additional interphase formation or initial decomposition at the Li1.5La1.5TeO6 interface, as observed in other solid-state electrolyte systems\(^6\)–\(^7\).

Discussion
We have demonstrated that the tungsten and tellurium analogues of the Li-rich double perovskite family, Li1.5La1.5MO6, are excellent candidate electrode and solid-electrolyte materials, respectively, for Li-ion batteries. The presence of Li ions in both A and B sites within the double perovskite framework enables Li-ion motion, and tailoring of the B-site cation directs the functionality towards a low-voltage negative electrode (Li1.5La1.5WO6) or a solid-state electrolyte (Li1.5La1.5TeO6). A detailed investigation into the redox mechanism of these materials unveils W\(^6+\) as the redox active species during Li insertion, whilst Te\(^6+\) confers a high redox stability, beyond 5 V, onto the perovskite crystal structure enabling its use as a safe alternative solid-state electrolyte. The promising diffusion properties of this new solid-electrolyte family presents an exciting opportunity for further performance optimisation through microstructure engineering and chemical composition exploration, reminiscent of previous oxide systems such as the Li-rich garnets or NASICON phases\(^6\)–\(^7\),\(^5\). Interestingly, the combination of both Li-rich double perovskites into a single hybrid solid-state cell retains the electrode functionality and paves the way for tailored
isostructural design of solid-state battery components whereby interface compatibility can be finely tuned at the unit cell level.

Methods

All reagent-grade chemicals employed for the synthesis of the Li-rich double perovskites were purchased from the following suppliers and used without further purification unless otherwise noted: LiOH·H2O (98%) and La2O3 (99%) from Sigma Aldrich, WO3 (99.95%) and TeO2 (99.978%) were purchased from Alfa Aesar.

For the microwave-assisted synthesis of the Li1.5La1.5WO6, Li1.5La1.5TeO6 and Li1.5La1.5TeO6 double perovskites, stoichiometric amounts of La2O3 (previously dried at 900 °C for 24 h), WO3, and/or TeO2, and a 10% excess of LiOH·H2O for NPD studies were ball milled for 30 min at a vibration frequency of 20 Hz in a stainless-steel jar. Subsequently, the fine powder was pelleted under uniaxial load of 3 t. The pellet material was then removed from the die, the surface graphite removed, and the pellet and sample used for x-ray powder diffraction (XRD) and Rietveld refinements.

Impedance Analyzer in the frequency range of 1 Hz to 7 MHz with a 50 mV voltage perturbation. Gas deposition was employed to sputter coat electrodes in Pt using a Polaron SC7640 with a sputtering time of 200 s, a current of 20 mA and an Ar pressure of 0.4–0.02 mbar. The same pellet was used for measurements with lithium electrodes, whereby the pellet was polished to remove the Pt coating and transferred to an Ar-filled glovebox. The pellet was sandwiched between two lithium foils (Sigma Aldrich, 0.38 mm) and assembled within a Swagelok cell. The surface of each lithium foil was scraped using a stainless-steel blade to ensure optimal contact with the pellet.

Density values were obtained through helium gas displacement pycnometry using a Micromeritics Accupyc II 1340 system. Raman data were acquired in a Horiba Jobin Yvon LabRAM HR system equipped with a Ventus 532 laser. Spectra were acquired in the 50–4000 cm−1 region with a 532 nm wavelength laser with a 100 mW power. The light beam was masked to the appropriate level in order to obtain data intensity in a measurable range.

The XAS data were collected in the B18 beamline at Diamond Source of Light synchrotron. For the data acquisition, a few milligrams (between 10 and 100 mg) of the sample in 300 µm diameter and 1.5 mm thickness. AC impedance and galvanostatic cycling measurements were performed in an FCT HP D 25 SPS furnace. Powder samples were loaded into a cylindrical graphite die with a 16-mm-inner diameter, lined with thin graphite foil. Rapid heating was controlled by a thermocouple inserted within the die for the duration of the experiment. The set-up was held under constant uniaxial pressure of 50 MPa whilst DC current pulses were used to heat the sample at a constant rate of C/mm² to 790 °C.

The target temperature was 1090 °C with a dwell time of 5 min once this was reached. After the experiment, the sample was allowed to cool naturally. The material was then removed from the die, the surface graphite removed, and polished. An additional sputter coating of 100 nm was used over 300 µm diameter and 1.5 mm thickness. AC impedance and galvanostatic cycling measurements of SPD samples were performed on a Biologic VSP potentiostat in the frequency range of 1 Hz to 7 MHz with a 50 mV voltage perturbation. Gas deposition was employed to sputter coat electrodes in Pt using a Polaron SC7640 with a sputtering time of 200 s, a current of 20 mA and an Ar pressure of 0.4–0.02 mbar. The same pellet was used for measurements with lithium electrodes, whereby the pellet was polished to remove the Pt coating and transferred to an Ar-filled glovebox. The pellet was sandwiched between two lithium foils (Sigma Aldrich, 0.38 mm) and assembled within a Swagelok cell. The surface of each lithium foil was scraped using a stainless-steel blade to ensure optimal contact with the pellet.

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Received: 23 September 2019; Accepted: 27 October 2020; Published online: 15 December 2020

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**Acknowledgements**

The authors gratefully acknowledge technical support from Michael Beglan and Peter Chung at the University of Glasgow. The authors also thank the EPSRC for grant funding (SUPERGEN Challenge grant on “Design and high throughput microwave synthesis of Li-ion battery materials”, EP/N001982/1); the support of the Faraday Institution (SOLBAT, Grant No. FIBGB007); the STFC for beamtime allocation through the GEM, Polaris and EMU beamlines at the ISIS neutron and muon source and the Diamond Light Source for XAS beamtime through the Energy Materials Block Allocation Group organised by Alan Chadwick and Giannantonio Cibin (proposal 25120); computational facilities such as the ARCHER supercomputer through membership of the UK’s HPC Materials Chemistry Consortium (funded by EPSRC Grants EP/L000202/1 and EP/R029431/1), the “Hydra” High Performance System at Loughborough University and the use of Athena as part of the HPC Midlands + consortium (EPSRC, EP/P020232/1); the Universities of Sheffield, Glasgow, Strathclyde and Loughborough for support and the use of facilities; and the School of Chemistry at Glasgow for PhD studentship funding.

**Competing interests**

The authors declare no competing interests.

**Additional information**

**Supplementary information** is available for this paper at https://doi.org/10.1038/s41467-020-19815-5.

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