Supporting Information

The XRD result shows that the film is mainly composed of LiV$_3$O$_8$ crystals with their [100] direction perpendicular to the substrate. Even though the film is uniform and close-packed, some scattered nanorods can be observed on the surface of the film as shown by the arrows in supplementary data Fig.S1. The nanorods are 150 nm long and 50 nm wide. The combination of the XRD results with supplementary data Fig.S1 demonstrate that the film is mainly composed of nanorods with (100) planes parallel to the substrate and (010) or (001) planes perpendicular to the substrate. The size of most crystals is about 50 nm wide and approximately 150 nm long.

Figure S1 SEM image of the surface morphology of the nanostructured LiV$_3$O$_8$ thin film. Some random nanorods are indicated by the arrows.
The further evidence for composition of amorphous wrapping is revealed by the TEM measurements. As we mentioned in the main text, the amorphous wrapping is metastable and a crystallization process occurs after continuous exposure to the electron beam. Fortunately, the transformation process can be clearly observed during the TEM measurement and the result is shown in supplementary data Fig.S2. Lattice fringes gradually appeared in the amorphous wrapping layer region and the spacing was measured to be 1.81 nm. This value agrees well with the spacing of (020) planes of the layered monoclinic LiV$_3$O$_8$. The TEM result indicates that the amorphous wrapping is composed of LiV$_3$O$_8$.

![Figure S2 High-resolution TEM image of the amorphous wrapping after continuous exposure to the electron beam](image)
Supplementary data figure S3 shows the XRD patterns of the LiV$_3$O$_8$ film deposited at different values of the sputtering oxygen partial pressure. There is no diffraction peak except for the substrate formed in a sputtering atmosphere of pure Ar, indicating that the main component of the film is amorphous. After increasing the ratio of Ar to O$_2$ in the gas mixture to 2:1, the crystalline component of the film is clearly LiV$_3$O$_8$ with no peaks associated with impurity phases. When altering the ratio of Ar/O$_2$ to 1:1, additional diffraction peaks are observed in the film and the Li$_{1.03}$V$_2$O$_5$ phase is observed. Overall, the crystallinity of the LiV$_3$O$_8$ film is enhanced with the increase of oxygen partial pressure. Supplementary data figure S4 shows the SEM image of the LiV$_3$O$_8$ thin film deposited with an Ar/O$_2$ ratio of 2:1. This shows particles 400 nm long with no heteropic compounds between them. The SEM image confirms that the crystallinity and particle size increase as a function of oxygen partial pressure.

Figure S3 XRD pattern of as-deposited LiV$_3$O$_8$ thin film with different sputtering oxygen partial pressures (a) pure Ar, (b) Ar:O$_2$=2:1 and (c) Ar:O$_2$=1:1.

Figure S4 SEM image of LiV$_3$O$_8$ thin film prepared by RF sputtering at an Ar/O$_2$ ratio of 1:1.
Supplementary data figure S5 illustrates the evolution of the charge/discharge profile of LiV$_3$O$_8$ with its amorphous wrapped nanorods structure at both fast-charging and the normal-discharging rate. It is clear that even when the polarization becomes more pronounced when the charging rate increases to 20 C, the film still retains a high discharge capacity of 250 mAh g$^{-1}$ at C/5. The rate performance is superior to all previous reports on LiV$_3$O$_8$ films.

Figure S5 Charge/discharge curve for LiV$_3$O$_8$ with amorphous wrapped nanorod structure at fast-charging and normal-discharging rate.

An Arrhenius plot of ln(D$_{Li^+}$) as a function of 1/T is shown in supplementary data figure S6. According to solid state diffusion theory, the activation energy can be calculated from the well-known Arrhenius equation:

$$D_{Li^+} = A \exp\left(-\frac{E_a}{RT}\right)$$

(1)

where $A$ is a temperature-independent coefficient, $E_a$ is the activation energy, $R$ is the gas constant (8.314 J·mol$^{-1}$·K$^{-1}$) and $T$ is the absolute temperature. $E_a$ is obtained from the slope of the linear fit of lnD$_{Li^+}$ against the reciprocal temperature, using the followed equation:
According to equation 2, the activation energies of LiV$_3$O$_8$ with the amorphous wrapped nanorod structure at 2.8 V and 2.4 V are 73.3 and 65.7 kJ mol$^{-1}$, respectively, values which are lower than those of the mixed microstructure LiV$_3$O$_8$ electrode. The lower activation energies for LiV$_3$O$_8$ indicate the presence of shorter diffusion routes for Li ions intercalation.

![Figure S6 Arrhenius plots of ln(D$_{Li^+}$) versus 1/T for (a) amorphous wrapped nanorods and (b) mixed microstructure LiV$_3$O$_8$ thin film](image)

Figure S6 Arrhenius plots of ln(D$_{Li^+}$) versus 1/T for (a) amorphous wrapped nanorods and (b) mixed microstructure LiV$_3$O$_8$ thin film