La_{1-x}K_xFeO_3_{3-x}: An Anion Intercalative Pseudocapacitive Electrode for Supercapacitor Application

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ABSTRACT: The green energy alternative to a fossil fuel-based economy can be provided only by coupling renewable energy solutions such as solar or wind energy plants with large-scale electrochemical energy storage devices. Enabling high-energy storage coupled with high-power delivery can be envisaged through high-capacitance pseudocapacitor electrodes. A pseudocapacitor electrode with multiple oxidation state accessibility can enable more than 1e^- charge/transfer per molecule to facilitate superior energy storage. K-doped LaFeO_3 (La_{1-x}K_xFeO_3_{3-x}) is presented here as an electrode having a high pseudocapacitance storage, equivalent to 1.32F/g at 1 mV/s scan rate by introduction of a layered potential over the Fe-ion octahedral to utilize higher redox state energies (Fe^{4+}→Fe^{2+}). La/K ordering in orthorhombic perovskite (La_{1-x}K_xFeO_3_{3-x}) made the Fe^{3+} oxidation state accessible, and a systematic shift in the redox energies of Fe^{4+/3+} and Fe^{3+/2+} redox couples was observed with K^+ ion doping in the A site of the LaFeO_3 perovskite, which resulted in a high faradic contribution to the capacitance, coupled with anionic intercalation of H_2O/OH^- in the host perovskite lattice. The surface capacitive and diffusion control contributions for capacitance are about 42 and 58%, respectively, at ~0.6 V, with a scan rate of 1 mV/s. A high gravimetric capacitance, equivalent to 619, 347, 188, 121, and 65 F/g, respectively, at 1, 2, 3, 5, and 10 A/g constant current, was observed for the La_{0.5}K_{0.5}FeO_3_{3-δ} electrode. Up to 88.9% capacitive retention and 97% Coulombic efficiency were obtained for continuous 5000 cycles of charge/discharge for the La_{0.5}K_{0.5}FeO_3_{3-δ} electrode. The gravimetric capacitance values of ASCs (activated carbon//La_{0.5}K_{0.5}FeO_3_{3-δ}) are 348, 290, 228, and 147 F/g at current densities of 1, 2, 3, and 5 A/g, respectively. A maximum specific power of ~3594 W/kg was obtained when the specific energy reached ~117 Wh/kg at 5 A/g of current density.

1. INTRODUCTION

To move away from fossil fuel-based energy solution and to produce power and electricity through the renewable energy generated through sources like solar, wind, and tidal energy, a large-scale electrochemical energy storage system is required.1-2 Electrochemical energy storage devices such as batteries and electrochemical capacitors are empowering portable electronics and broad-range electricity transmission through grid regulation and the transport sector.3 An electrochemical cell is generally made of two electrodes separated by an electrolyte (a high-ionic conductor made of aqueous and nonaqueous materials). As per the charge storage mechanism, electrochemical energy storage (EES) systems are classified into three categories: (a) electric double-layer capacitors (EDLCs) (containing carbon-based material, due to its high conductivity and high surface area available to adsorb electrolyte ions onto the surfaces to form an electric double-layer charge storage through electrified material15), (b) batteries (storing electrical energy as chemical energy in two electrodes: a reductant (anode) and an oxidant (cathode), separated by an electrolyte that allows transport of the ionic component of the chemical reaction for storage inside the electrode material16); (c) pseudocapacitors (in addition to having an electrostatic electric double layer, they store electrical energy in a faradic component, resulting normally from a shallow insertion of the mobile ions of the electrolyte into an electrode host with the reduction of host-electrode cations17). The E vs t plot behavior for the EDLC (surface charge storage) is linear, for the battery (faradic reaction) it is nonlinear, and for the pseudocapacitor (combination of faradic and surface charge storage) it is more linear compared to the battery.3,9 RuO_2 was the first extensively studied material to show pseudocapacitance behavior and continues to be an excellent capacitance material due to its high chemical stability and conductivity.10 However, its scarcity and high cost limit its application for commercial purposes, and as an alternate, MnO_2 was...
demonstrated to possess pseudocapacitive behavior.\textsuperscript{11} Vigorous studies have started on transition metal oxide-based materials such as NiO, V₂O₅, spinel Co₃O₄, Fe₂O₃, and mixed spinel NiCo₂O₄ to explore them as electrodes of a pseudocapacitor.\textsuperscript{12–18} Perovskite-type LaMnO₃ was demonstrated as an anion-intercalation pseudocapacitor.\textsuperscript{19} Perovskite oxides have the unit cell formula ABO₃, where the A-site is either an alkaline or lanthanide element, while the B-site is a transition metal element. By strategically selecting the A-site elemental composition, one can readily control the B-site oxidation state as well as the overall oxygen vacancy content via charge compensation.\textsuperscript{20,21} Perovskite supercapacitors have attracted widespread attention, and several perovskites such as LaNiO₃,\textsuperscript{22} LaFeO₃,\textsuperscript{23,24} La₃Sr₁−ₓCuxO₄,\textsuperscript{25} Sr₂CoMoO₆,\textsuperscript{26} and La₀.₈₅Sr₀.₁₅MnO₃\textsuperscript{27} were investigated for pseudocapacitance applications.

Perovskites are a very important class of electronic materials, especially layered perovskites such as YBa₂Cu₃O₇,\textsuperscript{28} La₂₋ₓBaₓCuO₄,\textsuperscript{29} La₃₋ₓCnxNb₂O₇,\textsuperscript{30} YBa₃Cu₅O₁₅,\textsuperscript{30} and La₂₋ₓSrₓMnO₃.\textsuperscript{26} Orthorhombic perovskites crystallize in orthorhombic perovskite structure, where an alternate layer of Y and Ba induces an interplanar potential that generates cooper pairs, and stabilizes the Cs⁺ ion in the B-site octahedral responsible for the high-temperature superconducting properties of the materials. The effect of internal field was also presented in the layered perovskite Na₄LnTiO₆ (Ln = La, Tb), where the internal potential generated over the Ti octahedral resulted in a systematic shift in the redox energy of Ti⁴⁺/³⁺ couples.\textsuperscript{31} Similarly, here, we envisaged the concept of accessing higher redox energies though incorporation of an internal layer potential to achieve multiple electron transfer, such as Fe⁴⁺ → Fe³⁺, for higher pseudocapacitive energy storage. In this manuscript, we have investigated the concept of layered potential on a transition metal-ion octahedral to utilize high redox energies (higher oxidation states such as Fe⁴⁺/²⁺) for fabrication of high-capacity electrodes. Using La/K ordering in orthorhombic perovskite (La₁₋ₓKₓFeO₃₋δ), the Fe⁴⁺ oxidation state is accessed and a systematic shift in redox energy (Fe⁴⁺/³⁺ and Fe³⁺/²⁺) with K⁺ ion doping on the A site of LaFeO₃ perovskite is shown, and in turn, a high pseudocapacitance of the electrode is demonstrated. A specific capacitance of 662 F/g, equivalent to 1.32e⁻/mole charge transfer, was observed for La₀.₅K₀.₅FeO₃₋δ in aqueous 2 M KOH electrolyte in a voltage window of 1 V. The detailed synthesis, characterizations, and electrochemical performance of La₁₋ₓKₓFeO₃₋δ are presented in this manuscript.

2. EXPERIMENTAL DETAILS

2.1. Materials Synthesis and Characterizations. The solid-state ceramic synthesis route was utilized to synthesize crystalline K-doped La₁₋ₓKₓFeO₃₋δ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) because this route in general produces more thermodynamically stable compounds. La₂O₃ (99.9%), K₂CO₃ (99.9%), and Fe₂O₃ (99.9%) were taken as precursors for the synthesis of the materials. The precursors were taken in stoichiometric ratio and mixed in an agate mortar pestle for about 30 min. The mixture was then fired in a platinum crucible at 1050 °C for 12 h for the preparation of LaFeO₃ and at 1150 °C for 12 h for the preparation of La₁₋ₓKₓFeO₃₋δ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5), followed by slow cooling to room temperature. Multiple heating and grinding of the samples were carried out to get single-phase materials. The phase formation was studied using a Rigaku MiniFlex desktop X-ray diffractometer (XRD) with Cu Kα radiation (λ = 1.54 Å) in the range 2θ = 20–90° with a step size of 0.02°. The structures were refined by the Rietveld refinement method using FULLPROF suite software, and orthorhombic perovskite (Pnma, space group 62) was taken as the model structure. The microstructures of the sintered samples were investigated using scanning electron microscopy (EVO—Scanning Electron Microscope MA15/18). The average grain size was calculated using the linear intercept method with ImageJ software. Pore-size distribution and specific surface area of the sample were measured by BET (Micromet.BEL).

X-ray photoelectron spectroscopy (XPS) studies were carried out to investigate the electronic structures of the materials. XPS of the sample was carried out using a Thermo Scientific Multilab 2000 instrument with Al Kα radiation operated at 150 W. The binding energies reported here are with reference to C (1s) at 284.5 eV, and they are accurate within ±0.1 eV. The oxidation state of Fe and oxygen stoichiometry were determined by chemical analysis using a redox titration method called iodometry. Twenty milligrams of active materials was dissolved in 30 mL of hydrochloric acid (3 M) in the presence of 24 mg of potassium iodide (KI), and the liberated iodine was titrated with sodium thiosulfate Na₂S₂O₃ (1 M) using starch as indicator. Concordant results for oxygen stoichiometry were obtained within an error of ±0.01. High-purity argon gas was bubbled into the solution to avoid oxygen contamination from air, and double-distilled preheated water was used in titration to avoid any dissolved oxygen contamination and active bacteria present in the water.

2.2. Electrochemical Studies. The electrochemical measurements were carried out using NOVA 2.0 autolab. The catalyst ink was prepared by homogenizing 35 mg of catalyst, 10 mg of acetylene black, and 5 mg of PVDF binder in 1 mL of NMP solvent under an ultrasonication bath for 40 min. To investigate the activity of the supercapacitance, an aliquot of 20 μL of homogenized ink was deposited by a micropipette onto the surface of a carbon paper (torrey carbon paper, alfa Aesar) (1 cm × 1 cm area) and dried under an IR lamp. The electrode loading was calculated by taking the weight of the electrode using an electronic balance (error limit: 0.01 mg). For that, first, the weight of the Torrey paper was taken; then, the weight of the coated electrode (after drying the coated ink on Torrey carbon paper of 1 × 1 cm² area) was taken for the study. Then, from the difference in the weights, the exact loading of the electrode material was calculated. The total material load was typically 1 mg (0.7 mg active material/ carbon/PVDF binder).

Cyclic voltammetry (CV), galvanometric charge/discharge, and electrochemical impedance spectroscopy (EIS) in a conventional three-electrode arrangement were used to determine the electrochemical characteristics of the prepared pseudocapacitor by a Metrohm Autolab (PGSTAT204) equipped with FRA32M module. Electrochemical measurements were analyzed using NOVA 2.0 software.

Pt was used as the counter electrode and Hg/HgO (1 M KOH) was utilized as the reference electrode. All electrodes were measured in 2 M KOH electrolyte; cyclic voltammetry (CV) was used to show redox behavior; chronopotentiometry was used for charge—discharge capacity measurements; and EIS was employed for the overall internal resistance measurements.
Figure 1. (a) XRD pattern of $\text{La}_{1-x}\text{K}_x\text{FeO}_3-\delta$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$), (b) Rietveld refinement of $\text{La}_0.5\text{K}_0.5\text{FeO}_3-\delta$, (c) structure of $\text{La}_0.5\text{K}_0.5\text{FeO}_3-\delta$, and (d) Jahn–Teller distortion over Fe–O octahedra in orthorhombic $\text{La}_0.5\text{K}_0.5\text{FeO}_3-\delta$ structure.

Figure 2. XPS of $\text{La}_0.5\text{K}_0.5\text{FeO}_3-\delta$ of the powder sample: (a) full survey, (b) Fe (2p) core level, (c) O (1s), (d) La (3d), and (e) K (2p). (f) $\text{N}_2$ adsorption–desorption isotherms with pore-size distribution.
3. RESULTS AND DISCUSSION

The XRD pattern of the prepared materials treated at 1150 °C for 12 h is shown in Figure 1a for La$_{1-x}$K$_x$FeO$_{3-δ}$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$). All of the synthesized materials show a single-phase formation. The prominent single-phase diffraction peak matches well with JCPDS file: 1526450. The Rietveld refined XRD profile of La$_0.5$K$_0.5$FeO$_{3-δ}$ is provided in Figure 1b. Rietveld refinement studies of La$_{1-x}$K$_x$FeO$_{3-δ}$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) show that all materials adopted an orthorhombic (Pnma, space group 62) type structure. The structure parameters derived from Rietveld refinement are presented in Table S1 (Supporting Information). Figure S1 (Supporting Information) shows that the (002) peak (highest-intensity peak) shifted linearly to a lower 2θ value with increasing dopant (K) concentration on the La site. As the ionic radii of K$^+$ (1.64 Å, 12 coordination) is greater than that of La$^{3+}$ (1.36 Å, 12 coordination),$^{35}$ doping of K on the La site will result in the peak shifting to a lower 2θ value. In the orthorhombic cell, large percentages of La ion were replaced by K ion; this may have resulted in the formation of the La and K alternating layer as shown in Figure 1c. The alternating layer of La and K can build a charge potential over the Fe–O octahedra, resulting in a tilt in the bond angle, and elongation in the nonplanar bonding, resulting in a Jahn–Teller type structural distortion of the Fe–O octahedral as shown in Figure 1d (vista image). This distortion favors the in situ formation of Fe$^{4+}$ (electronic configuration: t$_2g^3e_g^1$) to support the Jahn–Teller distortion. Thus, this internal potential affects or shifts the redox energy of Fe in such a way that Fe$^{4+}$/3+ and Fe$^{3+}$/2+ redox couples can become accessible to facilitate the superior pseudocapacitive storage capacity of the materials.

The survey spectra of the La$_0.5$K$_0.5$FeO$_{3-δ}$ sample containing (C 1s), O (1s), Fe (2p), La (3d), K (2s) (377.41 eV),$^{33}$ and K (2p) (293.16 eV)$^{33}$ are shown in Figure 2a. To investigate the Fe oxidation state, XPS of the core-level Fe (2p) spectra of La$_0.5$K$_0.5$FeO$_{3-δ}$ and LaFeO$_3$ samples is shown in Figure 2b. The XPS curve is fitted or deconvoluted with the help of XPSPEAK41 software. The peak position indicates that only the Fe$^{3+}$ state is present in LaFeO$_3$ and both Fe$^{3+}$ and Fe$^{4+}$ states are present in La$_0.5$K$_0.5$FeO$_{3-δ}$. For the Fe$^{3+}$ oxidation state, binding energies were obtained at 709.95 eV (2p$_{3/2}$) and 723.74 eV (2p$_{1/2}$), and for the Fe$^{4+}$ oxidation state, binding energies were obtained at 712.65 eV (2p$_{3/2}$) and 726.2 eV (2p$_{1/2}$) with the presence of a weak satellite peak at 718.40 eV.$^{34}$ The Fe (2p$_{3/2,1/2}$) spectra clearly depict the presence of Fe$^{4+}$ ion as the majority phase in La$_0.5$K$_0.5$FeO$_{3-δ}$. The ratio of Fe$^{4+}$ and Fe$^{3+}$ ions was calculated from their peak strength and found to be close to 2.92 ± 0.01. This suggests that the La$_0.5$K$_0.5$FeO$_{3-δ}$ sample contains 84% of Fe$^{4+}$ and 16% of Fe$^{3+}$. This study matches very well with the XPS study of the Fe oxidation state of our sample. Similarly, for the La$_0.7$K$_0.3$FeO$_{3-δ}$ sample, Fe$^{4+}$/Fe$^{3+}$ oxidation states were found to be in the ratio of 54:46, and the oxygen content was found to be 2.97.

The scanning electron microscope (SEM) image shown in Figure 3a presents the porous sphere-type particle morphology of the La$_0.5$K$_0.5$FeO$_{3-δ}$ sample. Particle-size distribution was calculated using ImageJ software and was fitted with Gaussian distribution. The particles’ diameters were found to be in the range of 0.856–1.38 μm, with an average particle diameter of about 1.3 μm. Figure 3b shows the high-resolution transmission electron microscopy (HRTEM) images of the sample. Lattice fringes are clearly visible in the inverse fast Fourier transform (FFT) (mapping with Gatan Digital micrograph software) of this region, confirming the crystalline nature of La$_0.5$K$_0.5$FeO$_{3-δ}$. The lattice fringe spacing is in agreement with the interplanar spacing obtained from the XRD results. The electrochemical performance of La$_{1-x}$K$_x$FeO$_{3-δ}$ ($x = 0, 0.3, 0.4, 0.5$) samples was determined from the cyclic N$_2$ adsorption–desorption isotherms with pore-size distribution are shown for LaFeO$_3$ and La$_0.5$K$_0.5$FeO$_{3-δ}$ in Figure 2f. The surface area for pure LaFeO$_3$ was found to be 19 m$^2$/g, and for La$_0.5$K$_0.5$FeO$_{3-δ}$ sample it was 26 m$^2$/g. Both samples show a large number of pores with a pore-size distribution between 2 and 12 nm diameter. Iodometry titrations were carried out to determine the oxygen stoichiometry of the La$_0.5$K$_0.5$FeO$_{3-δ}$ sample, and the oxygen content was found to be close to 1526450. The Rietveld refinement studies of La$_{1-x}$K$_x$FeO$_{3-δ}$ are presented in Supporting Information. Figure S1 (Supporting Information) shows that the (002) peak (highest-intensity peak) shifted linearly to a lower 2θ value with increasing dopant (K) concentration on the La site. As the ionic radii of K$^+$ (1.64 Å, 12 coordination) is greater than that of La$^{3+}$ (1.36 Å, 12 coordination),$^{35}$ doping of K on the La site will result in the peak shifting to a lower 2θ value. In the orthorhombic cell, large percentages of La ion were replaced by K ion; this may have resulted in the formation of the La and K alternating layer as shown in Figure 1c. The alternating layer of La and K can build a charge potential over the Fe–O octahedra, resulting in a tilt in the bond angle, and elongation in the nonplanar bonding, resulting in a Jahn–Teller type structural distortion of the Fe–O octahedral as shown in Figure 1d (vista image). This distortion favors the in situ formation of Fe$^{4+}$ (electronic configuration: t$_2g^3e_g^1$) to support the Jahn–Teller distortion. Thus, this internal potential affects or shifts the redox energy of Fe in such a way that Fe$^{4+}$/3+ and Fe$^{3+}$/2+ redox couples can become accessible to facilitate the superior pseudocapacitive storage capacity of the materials.

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Of the La$_0.5$K$_0.5$FeO$_{3-δ}$ sample. Particle-size distribution was calculated using ImageJ software and was fitted with Gaussian distribution. The particles’ diameters were found to be in the range of 0.856–1.38 μm, with an average particle diameter of about 1.3 μm. Figure 3b shows the high-resolution transmission electron microscopy (HRTEM) images of the sample. Lattice fringes are clearly visible in the inverse fast Fourier transform (FFT) (mapping with Gatan Digital micrograph software) of this region, confirming the crystalline nature of La$_0.5$K$_0.5$FeO$_{3-δ}$. The lattice fringe spacing is in agreement with the interplanar spacing obtained from the XRD results.
voltammetry and galvanistic charge/discharge curve. All samples of La$_{1-x}$K$_x$FeO$_3$−δ ($x = 0, 0.3, 0.4, 0.5$) were studied in a 2 M KOH electrolyte in the voltage range of 0 to −1 V. We performed the study up to −1 V because below that we observed oxygen reduction reaction (ORR) over our electrode, which creates loss of capacitance of the materials. Figure 4a represents the cyclic voltammetry curve for La$_{1-x}$K$_x$FeO$_3$−δ ($x = 0, 0.3, 0.4, 0.5$) with increasing K concentration. The Fe$^{4+/3+}$ and Fe$^{3+/2+}$ redox peaks appear shifted to a lower potential linearly. For example, in undoped LaFeO$_3$ the Fe$^{3+/2+}$ redox couple appears at −0.84 V, in La$_{0.7}$K$_{0.3}$FeO$_{3-δ}$ it appears at −0.64 V, and in La$_{0.5}$K$_{0.5}$FeO$_{3-δ}$ it appears at −0.59 V. Similarly, the Fe$^{4+/3+}$ couple appears at −0.85 V in La$_{0.7}$K$_{0.3}$FeO$_{3-δ}$ and at −0.89 V in La$_{0.5}$K$_{0.5}$FeO$_{3-δ}$, and did not appear up to −1 V for undoped LaFeO$_3$. Thus, the inductive internal potential arises due to alternation of La and K layers over the Fe−O octhedra (as shown in Figure 1c), which makes the Fe$^{4+/3+}$ redox couple accessible for electrochemical performances. The cyclic voltammetry curves for La$_{1-x}$K$_x$FeO$_3$−δ ($x = 0, 0.3, 0.4, 0.5$) with different scan rates

Figure 4. (a) Cyclic voltammetry of La$_{1-x}$K$_x$FeO$_3$−δ ($x = 0, 0.4, 0.5$) material at a scan rate of 10 mV/s in 2 M KOH electrolyte; (b–d) cyclic voltammetry of La$_{1-x}$K$_x$FeO$_3$−δ ($x = 0.3, 0.4, 0.5$) material in 2 M KOH electrolyte; and (e) plot of peak current density vs square root of the scan rates of the La$_{1-x}$K$_x$FeO$_3$−δ ($x = 0, 0.3, 0.5$) sample.
are shown in Figure 4b–d, respectively. For the x = 0.3 composition, La0.2K0.8FeO3.44FeO6.16O2.97, with almost equal concentrations of Fe4+ and Fe3+ states, both Fe4+/3+ and Fe3+/2+ redox peaks seem to operate in a very close voltage range, representing a clean diffusion-controlled behavior of the electrode. However, a low capacity output resulted for the La0.7K0.3Fe0.55O2.92 electrode. The quasi-rectangular shape of the curve suggests the dominance of pseudocapacitance behavior over EDLC. The specific capacitance C (F/g) was calculated to understand the electrochemical performance of the working electrode, as represented by eq 1.

\[ C_p = \frac{\int I(A) \, dV}{m \nu} \]  

(1)

where \( I(A) \) is the cathodic current, \( \nu \, (V/s) \) is the scan rate, \( m \) (g) is the mass of active material, and \( V \) (V) is the sweep potential window.35

The gravimetric capacitance of La1-xKxFeO3-δ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) materials from the cyclic voltammetry curve at a scan rate of 1 mV/s was found to be 95, 113, 143, 203, 394, and 662 F/g, respectively. The capacitance of La0.5K0.5FeO2.92 which contains almost 84% Fe in the Fe4+ oxidation state as confirmed by XPS and iodometry titration study, was found to be ~662 F/g, suggesting more than one electron or anion transfer per molecule. In aqueous KOH electrolyte with predominant OH− transportation, the redox reaction pseudocapacitive storage can be represented as

\[ \text{La}_{1-x}\text{K}_{x}\text{[Fe}^{4+}\text{Fe}^{3+}\text{]}\text{O}_{3-\delta} + 2ye^{-} + y\text{H}_{2}\text{O} \]

\[ \leftrightarrow \text{La}_{1-x}\text{K}_{x}\text{[Fe}^{3+}\text{}/^{2+}\text{]}\text{O}_{3-\delta-\delta}\text{[OH}^{-}\text{]}_{2y} \]  

(2)

Thus, formation of La1-xKx[Fe3+/2+]O3-δ(OH-)2y results in pseudocapacitance through OH− intercalation coupled with surface adsorption. For y = 0.5, with the intercalation of one OH− coupled with 1e− charge transfer, the theoretical capacity of La0.5K0.5FeO2.92 should be ~500 F/g and therefore with the observation of ~662 F/g capacity of the electrode, the equivalent charge transfer of 1.32e− or OH−/H2O transport/transfer takes place per molecule of La0.5K0.5FeO2.92.

Thus, for La0.5K0.5[Fe4+0.86Fe3+0.16]O2.92, the redox reaction can be represented as

\[ \text{La}_{0.5}\text{K}_{0.5}\text{[Fe}^{4+}\text{0.86Fe}^{3+}\text{0.16}]\text{O}_{2.92} + 1.32e^{-} + 0.66\text{H}_{2}\text{O} \]

\[ \leftrightarrow \text{La}_{0.5}\text{K}_{0.5}\text{[Fe}^{3+}\text{0.72Fe}^{2+}\text{0.28}]\text{O}_{2.36}\text{[OH}^{-}\text{]}_{3.2} \]  

(3)

To understand the electrochemical kinetics of the La1-xKxFeO3-δ (x = 0, 0.3, 0.5) sample, a plot of the anodic and cathodic peak currents with respect to the square root of the scan rate is plotted in Figure 4e. The linear fitting of these plots represents a semi-infinite diffusion-controlled process. The kinetics of the electrode can be examined with the help of the diffusion coefficient. Determination of the diffusion coefficient of those electrodes was done using Randles–Sevick equation.35

\[ i_p = 2.686 \times 10^5 \times n^{3/2}AD^{1/2}C_{p}\nu^{1/2} \]  

(4)

where \( i_p \) is the peak current (A), \( n \) is the number of electrons transferred in the redox event (usually 1), \( A \) is the electrode area in cm², \( D \) is the diffusion coefficient in cm²/s, \( C_{p} \) is the OH− ion concentration in mol/cm³, and \( \nu \) is the scan rate in V/s. The diffusion coefficients of OH− calculated using eq 4 at 1 mV/s are presented in Table 1. For La1-xKxFeO3-δ (x = 0, 0.3, 0.4, 0.5) anode materials, the forward reaction is a charging and backward reaction discharging process. During the charging process, \( \text{H}_2\text{O} \) and \( e^{-} \) react at the electrode surface with \( \text{OH}^{-} \) that are diffused through the surface to the lattice.37,38 During discharge, \( \text{H}_2\text{O} \) is exchanged through the lattice resulting in recreation of the initial structure.

The area under the curve from the CV plot represents the total charge stored through faradic and nonfaradic reactions occurring on the electrode surface. The current behavior generally follows the power law and is related to the scan rate by the following equation

\[ i = a\nu^{b} \]  

(5)

where a and b are the variables that govern the nature of intercalation, i is the current (A), and \( \theta \) is the scan rate (V/s).

Table 1. Determination of the Diffusion Coefficient

| sample          | the anodic peak current \( (D_i) \) (cm²/s) | the cathodic peak current \( (D_c) \) (cm²/s) |
|-----------------|------------------------------------------|------------------------------------------|
| LaFeO3          | \( 5.827 \times 10^{-8} \)                | \( 5.998 \times 10^{-8} \)                |
| La0.5K0.5FeO3-δ | \( 4.554 \times 10^{-7} \)                | \( 3.889 \times 10^{-7} \)                |
| La0.7K0.3Fe0.55O2.92 | \( 9.806 \times 10^{-7} \)                | \( 7.711 \times 10^{-7} \)                |

The value of \( b \) lies between 0.5 and 1, \( b = 0.5 \) stands for the diffusion control reaction or battery type behavior, and \( b = 1 \) stands for the diffusion control faradic process involving charge transfer with surface/subsurface atoms.39 The b values for the La0.5K0.5FeO3-δ sample were found to be varying linearly with the scan rates at different potentials ranging from ~0.2 to ~0.8 V as shown in Supporting Figure S2-a.b. As shown in Figure 5a, in the charging process of the anode material at ~0.4 V, the b value was found to be 0.57, suggesting the dominance of the diffusion control process; except at ~0.4 V, for other potentials the b values were found to be above 0.8, suggesting the dominance of the faradic process over surface couples’ redox-mediated capacitance behavior. Similarly, in the discharging process, b values were found to higher than 0.85, suggesting the redox pseudocapacitive process from charge transfer with surface/subsurface atoms (Supporting Figure S2-a,b). The b values for La0.5K0.5FeO3-δ electrode were varied differently in two different regions, (1) \( \leq 10 \text{ mV/s} \) and (2) \( \geq 10 \text{ mV/s} \), in the plot of the log(peak current \( (A) \)) vs log(scan rate (mV/s)) as shown in Figure 5b. The b values for cathodic and anodic diffusion are 1 and 0.98, respectively, below 10 mV/s, suggesting rapid surface control kinetics, and the b values for cathodic and anodic diffusion are 0.87 and 0.7 above 10 mV/s, suggesting a resistance at high scan rates.

Similarly, the voltammetry sweep rate dependence on the current response can distinguish the capacitive contribution to the current response quantitatively. The current response at a fixed potential is envisaged as the combination of two separate mechanisms, surface capacitive effects, and diffusion-controlled insertion.40,41

\[ i(\nu) = K_{\nu}\nu + K_{2}\nu^{1/2} \]  

(6)

For more understanding, eq 6 can be rearranged to

\[ \frac{i(\nu)}{\nu^{1/2}} = \frac{K_{1}}{\nu^{1/2}} + K_{2} \]  

(7)

\( K_{\nu} \) and \( K_{\nu}^{1/2} \) represent the current contributions from the surface capacitive effects and the diffusion-controlled intercalation process, respectively. Thus, after the determination of
The values of the electrode. It can be expressed as the sum of intercalative (inner) and outer surface capacitance respectively, at 100 mV/s as shown in Figure 5d. Control contributions were found to be 88 and 12%, rate; i.e., the surface capacitive contribution and diffusion control participation with different scan rates at the discharge peak potential (−0.96 V); and (e, f) Trasatti plot at a scan rate of 100 to 1 mV/s for the charge–discharge process.

According to Trassati, the total specific capacitance is the sum of intercalative (inner) and outer surface capacitance values of the electrode. It can be expressed as

$$C_{\text{total}} = C_{\text{in}} + C_{\text{out}}$$

The specific capacitance contributed from the inner and outer surfaces of the electrode is dependent upon the scan rate (Figure 5e). The y-intercept of the linear fit of the 1/q vs ν^1/2 plot at ν = 0 represents the total amount of charge stored in the electrode. In Figure 5f, the y-intercept of the linear fit of the q vs ν^1/2 plot at ν = ∞ corresponds to the amount of charge stored at the outer surface of the electrode. Applying the Trasatti plot outcome, it can be concluded that the total capacitance value (C_{total} = 662 F/g) of La_{0.5}K_{0.5}FeO_{3−δ} has an intercalative inner surface contribution (C_{in}) equivalent to 359 F/g and outer surface contribution (C_{out}) equivalent to 303 F/g.

The charge–discharge measurement (potential V vs time t) was carried out at a constant current by chronopotentiometry. The gravimetric capacitance value was calculated from the potential V vs time t plot by using the following equation

$$C = \frac{I \Delta t}{m \nu}$$

where I (A) is the applied constant current, Δt (s) is the discharge time, m (g) is the active mass, and V represents the operating potential window.

The gravimetric capacitance values of the La_{1−x}K_{x}FeO_{3−δ} (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) electrode from the charge–discharge plot are shown in Figure 6a, and at a current rate of 1 A/g their values were found to be 101, 117, 148, 226, 389, and 619 F/g, respectively. The gravimetric capacitance values in Figure 6c were found to be 619, 347, 188, 121, and 65 F/g, respectively, at 100 mV/s as shown in Figure 5d.

The electrochemical impedance spectroscopy (EIS) measurement was carried out at an applied AC voltage of 10 mV from 1 MHz to 0.1 Hz range and is shown by the Nyquist plot in

Figure 5. (a) b Values at different potentials of La_{0.5}K_{0.5}FeO_{3−δ} in the charging and discharging processes at different potentials; (b) plot of log(peak current) vs log(scan rate); (c) capacitive and diffusion control process of the La_{0.5}K_{0.5}FeO_{3−δ} electrode at 10 mV/s; (d) capacitive and diffusion control percentage with different scan rates at the discharge peak potential (−0.96 V); and (e, f) Trasatti plot at a scan rate of 100 to 1 mV/s for the charge–discharge process.
Figure 6e for the La$_{1-x}$K$_x$FeO$_{3-\delta}$ ($x = 0, 0.3, 0.4, 0.5$) electrodes. The specific impedance contribution is mainly attributed to the impedance distributions over the electric series resistance ($R_s$), charge transfer resistance ($R_{ct}$), and Warburg impedance ($R_w$). The higher frequency resistance of the La$_{1-x}$K$_x$FeO$_{3-\delta}$ electrode gradually decreases with increasing K ion substitution in the sample, as the electronic conductivities of the samples increase with increasing K doping. The lower-frequency data represent the Warburg diffusion resistance, and for La$_{1-x}$K$_x$FeO$_{3-\delta}$ ($x = 0, 0.3, 0.4, 0.5$) samples, the straight line in the low-frequency region is close to 90° (very close to the $-Z''(\Omega)$ axis) and the horizontal line represents the characteristic of pseudocapacitance behavior of the La$_{0.5}K_{0.5}$FeO$_{3-\delta}$ electrode. This also represents fast OH$^-$ ion diffusion in the porous structure.

**Two-Electrode Test.** To understand the real charge storage behavior of La$_{0.5}K_{0.5}$FeO$_{3-\delta}$ relative to AC (activated carbon), two-electrode ASC (asymmetry supercapacitor) measurements have been conducted in 2 M KOH. To determine the maximum specific capacitance during full test, the storage capacity of the positive and negative electrodes needs to be balanced as per the following equation.
For balancing the charge storage capacity of the cell, the mass ratio ($m^+ / m^-$) of the positive and negative electrode materials was measured using the following equation

$$\frac{1}{C_{\text{total}}} = \frac{1}{C^+} + \frac{1}{C^-}$$  \hspace{1cm} (10)

For balancing the charge storage capacity of the cell, the mass ratio ($m^+ / m^-$) of the positive and negative electrode materials was measured using the following equation

$$m^+ = \frac{C^+ \Delta E^- \gamma}{C^- \Delta E^+ \gamma}$$  \hspace{1cm} (11)

where $m^+$, $m^-$, $C^+$, $C^-$, $\Delta E^+$, and $\Delta E^-$ are the mass, specific capacitance, and potential window of the positive and negative electrodes, respectively, estimated by the three-electrode measurement.36,37

Figure 7a shows the CV at 10 mV/s scan rate where the used AC (activated carbon) acts as the positive electrode and $\text{La}_{0.5}\text{K}_{0.5}\text{FeO}_{3-\delta}$ acts as the negative electrode. The calculated mass ratio ($m^+ / m^-$) was found to be 1.223 for the asymmetric cell, and the weight of the active materials was taken to be 3.3 mg (excluding the weight of acetylene black and PVDF). Figure 7b demonstrates the CV curve of the two electrodes $\text{La}_{0.5}\text{K}_{0.5}\text{FeO}_{3-\delta}$//AC in ASC mode at different scan rates, ranging from 1 to 100 mV/s in the potential window of 2 V, to assess the possible change in the oxidation state of Fe from Fe$^{2+}$ to Fe$^{4+}$. Figure 7c shows the charge–discharge curve plotted for measuring the capacitance of the electrode; the capacitance value was calculated using eq 9. The capacitance values for the $\text{La}_{0.5}\text{K}_{0.5}\text{FeO}_{3-\delta}$ electrodes were found to be 348, 290, 228, and 147 F/g at current densities of 1, 2, 3, and 5 A/g, respectively. Figure 7d shows the EIS plot (Nyquist) in the frequency range 1 MHz to 0.1 Hz at 10 mV applied voltage, confirming the superior charge transfer and higher capacitance of $\text{La}_{0.5}\text{K}_{0.5}\text{FeO}_{3-\delta}$//AC in full-cell mode. Figure 7e shows that the Coulombic efficiency of the two-electrode full cell is reduced only by 3%, with a higher capacity retention close to 90.5% of its initial value after 2000 cycles at a constant current of 5 A/g. The specific energy and specific power of the asymmetric capacitors were calculated using the following equations

$$E (\text{Wh/kg}) = \frac{1}{2} C_{\text{ASCs}} V^2$$  \hspace{1cm} (12)

$$P (\text{W/kg}) = \frac{E \times \text{3600}}{t_{\text{dis}}$$  \hspace{1cm} (13)

where $C_{\text{ASCs}}$ is the specific capacitance, $V$ is the operating voltage, and $t_{\text{dis}}$ is the discharge time.37

Figure 7f shows the plot of specific energy vs specific power with different constant current rates. The resultant values show the highest specific energy of 193 Wh/kg at 1 A/g current density and a specific power of ~1004 W/kg. The maximum specific power of ~3594 W/kg was obtained when the specific energy was reduced to ~117 Wh/kg at 5 A/g current density.

**CONCLUSIONS**

In summary, it can be concluded that by using an induced interlayer potential by altering the La$^3+$ and K$^+$ layer in $\text{La}_{1-x}\text{K}_x\text{FeO}_{3-\delta}$, Fe$^{4+/3+}$ and Fe$^{3+/2+}$ redox energies can be tuned and made accessible to envisage a higher capacity (662 F/g equivalent to 1.32 e$^-$/OH$^-$ diffusion) for the $\text{La}_{0.5}\text{K}_{0.5}\text{FeO}_{3-\delta}$ electrode. The higher $b$ values (>0.8) obtained for the diffusion-controlled reaction suggest a high faradic pseudocapacitive contribution to the electrode. Even with the Trassati plot, a higher degree of inner layer contribution, 54% ($C_{\text{in}} = 359$ F/g), to the total capacitance ($C_{\text{total}} = 662$ F/g) was obtained for the $\text{La}_{0.5}\text{K}_{0.5}\text{FeO}_{3-\delta}$ electrode. Up to 88.6% capacitive retention and Coulombic efficiency (95%) was
obtained after continuous 5000 cycles of charge/discharge, and a maximum specific power of ~3594 W/kg was obtained when the specific energy reached ~117 Wh/kg at 5 A/g of current density for the La$_{0.5}$K$_{0.5}$FeO$_{3-δ}$ electrode in the two-electrode La$_{0.5}$K$_{0.5}$FeO$_{3-δ}$/AC full-cell mode, with the remarkable stability of the electrode making the La$_{0.5}$K$_{0.5}$FeO$_{3-δ}$ electrode suitable as a negative electrode for pseudocapacitor applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03902.

Enlarged image of powder XRD plot of La$_{1−x}$K$_x$FeO$_3$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) showing peak shifting of (002) diffraction peak; plot shows linear relationship of log(ν) vs log(δ), slope represent b value according to power law; and capacitive and diffusion control processes contribution can be distinguish from applying equation (PDF)

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Notes

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