Supporting information

A Low-overpotential Potassium-Oxygen Battery Based on Potassium Superoxide

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Experiment details

Swagelok cell assembly. Super P carbon powders (kindly provided by TIMCAL Ltd.) were ground with PTFE powders (Sigma Aldrich, 1 micron size) (weight ratio=1:1). A slurry was then formed when 0.5 M KPF_6 (Sigma Aldrich, 99.9%) solution in 1,2-dimethoxyethane (DME, Novolyte Tech.) or diglyme (Sigma Aldrich, 99.5%) was added. The slurry was casted into a Nickel foam disk (O.D.=12 mm, thickness=1.7 mm) to make a porous carbon air electrode. The Swagelok cell was assembled by stacking a potassium metal foil (Sigma Aldrich, 99.5%), a whatman glass fiber separator (saturated with 0.5 M KPF_6 in DME or diglyme electrolyte) and the air electrode together. The cell was O-ring (Macro Rubber, Viton) sealed except for valves introducing dried oxygen gas at one atm pressure. An artificial discharged battery was built with similar procedure except for that the slurry was a mixture of carbon powder, PTFE and KO_2 (Sigma Aldrich) (ratio=1:1:1). All solvents, including diethylene glycol dibutyl ether (butyl diglyme, Sigma Aldrich, >99%) and tetraglyme (Novolyte), were dried by 4A molecular sieves and cell assembly was conducted in a glove box filled with high purity Argon.

Electrochemical tests. Batteries were tested using a Maccor testing station (model: 4304), with discharge and charge current density at 0.16 mA/cm^2 (geometry area) and within a voltage range between 2.0 V and 3.2 V (vs. K^+/K). Oxygen reduction reactions were performed in the presence of 0.1 M of different salts, e.g. tetrabutylammonium hexafluorophosphate($TBAPF_6$, Sigma Aldrich, electrochemical grade), $LiClO_4$ (Alfa Aesar, electrochemical grade) and KPF_6, to study the influence of different cations. Cyclic voltammetry studies were carried out on a Gamry potentiostat in a three-electrode system, with a glassy carbon working electrode (3 mm diameter), a platinum wire counter electrode and a Ag^+/Ag nonaqueous reference electrode (10 mM $AgNO_3$ in Acetonitrile, from CHI Inc.). Acetonitrile was distilled with CaH_2 prior to use.

Characterization. After battery test, the air electrode was first washed with DME to get rid of residual conducting salt and then dried under vacuum. The structure of discharge product was characterized by X-ray diffractometer (Bruker D8 Advance, Cu-Kα source, 40 kV, 50 mA) using air-sensitive sample holder with a moisture barrier film. Raman spectrum of discharged air electrode was obtained on a microscope Raman spectrometer (inVia, Renishaw) at a 633 nm excitation wavelength (laser power 6 mW) using an air-sensitive sample holder with a ZnSe optical window. Side products in air electrode were extracted by D_2O (Sigma Aldrich, 99.9 atom % D) and tested by NMR (Bruker, 400 MHz)

Table S1. Thermodynamics of possible discharge reaction products in K-O_2, Na-O_2 and Li-O_2 batteries and corresponding specific capacity as well as energy density. (Data for Na-O_2 and Li-O_2 batteries got from reference 26 in the main text)

Product	Reaction	$\Delta_r S$ (J/(mol·K))	$\Delta_r H$ (kJ/mol)	$\Delta_r G$ (kJ/mol)	z	E^o (V)	Specific Capacity (mAh/g)	Energy Density (Wh/kg)
KO_2 [1]	$K + O_2 \rightarrow KO_2$	116.7	-284.9	-239.4	1	2.48	377.0	934.9
K_2O_2 [1]	$2\,K + O_2 \rightarrow K_2O_2$	102.1	-494.1	-425.1	2	2.20	486.4	1070.2
K_2O [2]	$2\,K + {}^1/_2\,O_2 \rightarrow K_2O$	94.1	-363.2	-322.2	2	1.67	569.1	950.3
NaO_2	$Na + O_2 \rightarrow NaO_2$	-140.6	-260.7	-218.8	1	2.27	488.2	1108.2
Na_2O_2	$2\,Na + O_2 \rightarrow Na_2O_2$	-212.9	-513.2	-449.7	2	2.33	689.0	1605.4
Na_2O	$2\,Na + {}^1/_2\,O_2 \rightarrow Na_2O$	-130.1	-415.1	-376.3	2	1.95	867.4	1691.4
Li_2O_2	$2\,Li + O_2 \rightarrow Li_2O_2$	-206.9	-632.5	-570.8	2	2.96	1168.3	3458.3
Li_2O	$2\,Li + {}^1/_2\,O_2 \rightarrow Li_2O$	-123.2	-597.9	-561.2	2	2.91	1793.9	5220.2

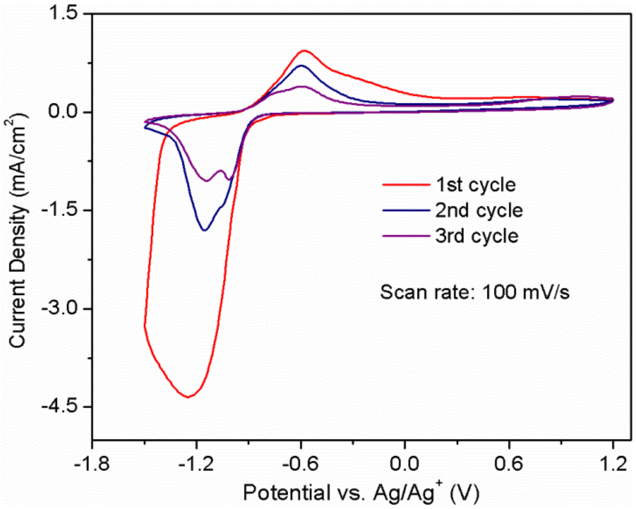

Figure S1. Cyclic voltammograms for oxygen reduction and oxidation on a glassy carbon electrode in oxygen saturated acetonitrile containing 0.1 M KPF_6.

Three subsequent cycles of oxygen reduction and oxidation with K^+ in MeCN were shown in Fig. S1. As indicated in Table S1, the difference between E° (O_2/KO_2) and E° (O_2/K_2O_2) is less than 0.3V, which indicates that the formation of K_2O_2 is feasible within the negative potential limit. The broad anodic shoulder peak around -0.2V (vs. Ag/Ag$^+$) also indicate that the complicated nature of reduction products. Meanwhile, the subsequent CV scans show two separated cathodic peaks, which supports this possibility of K_2O_2 formation. The low conductivity of K_2O_2, which is regarded as a wide band-gap semiconductor, could passivate the GC electrode.[3] Therefore the anodic current densities are smaller than the cathodic current densities and the currents decay with increasing cycle number.

The cathodic and anodic peaks are not clearly assigned now. The cyclic voltammograms are shown to prove our hypothesis that the redox chemistry of oxygen could be greatly influenced by the property of cations and be more reversible with potassium ions than with lithium ions. In practical battery tests, the negative polarization of the air electrode was limited close to the equilibrium potential (2.48 V), so that K_2O_2 formation was effectively eliminated (see Fig. 3).

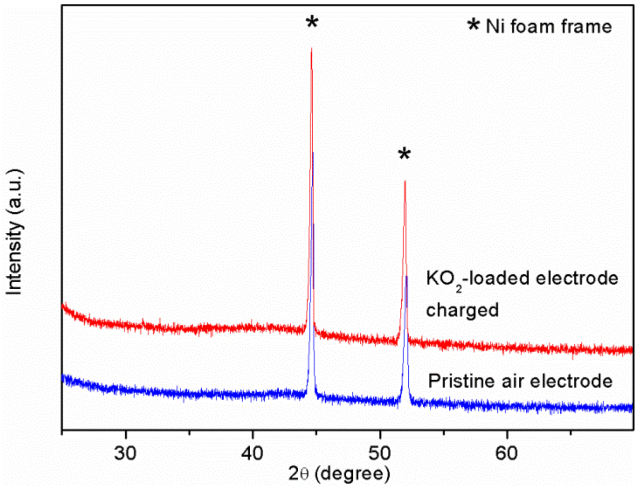

Figure S2. The XRD patterns of a pristine air electrode and a KO_2-loaded electrode after charging.

The peaks of KO_2 disappeared after the charge process. This indicates that KO_2 was oxidized in the process.

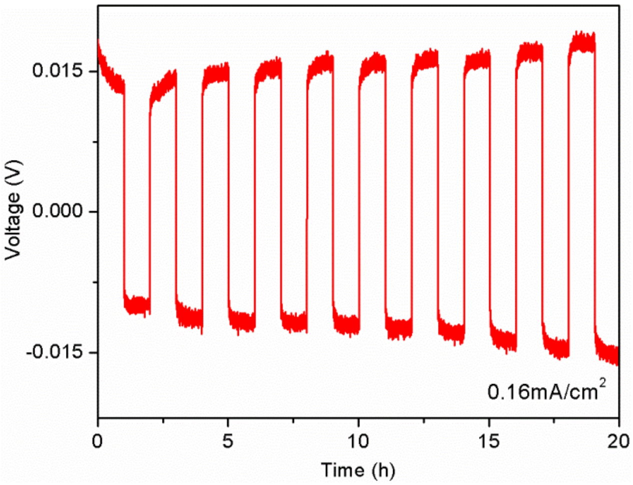

Figure S3. The voltage profile of potassium electrodeposition and dissolution at 0.16 mA/cm^2 in a K|K symmetric cell (0.5 M KPF_6 in butyl diglyme/ diglyme mixture with a volume ratio of 2:5).

Ether and polyether solvents are known to be able to coordinate to alkali metal ions and generate solvated electrons or metal anions.[4,5] These species are highly reductive in nature and may induce the decomposition of electrolyte. Tetraglyme was not used for K-O_2 batteries because of its very strong coordination ability to K^+.[6] Mixing butyl diglyme with diglyme (volume ratio=2:5) was found to stable with potassium metal by suppressing the co-ordination of ether molecules to potassium cations. This agrees with the theoretical study showing the main role of terminal oxygen atoms for the coordination.[7]

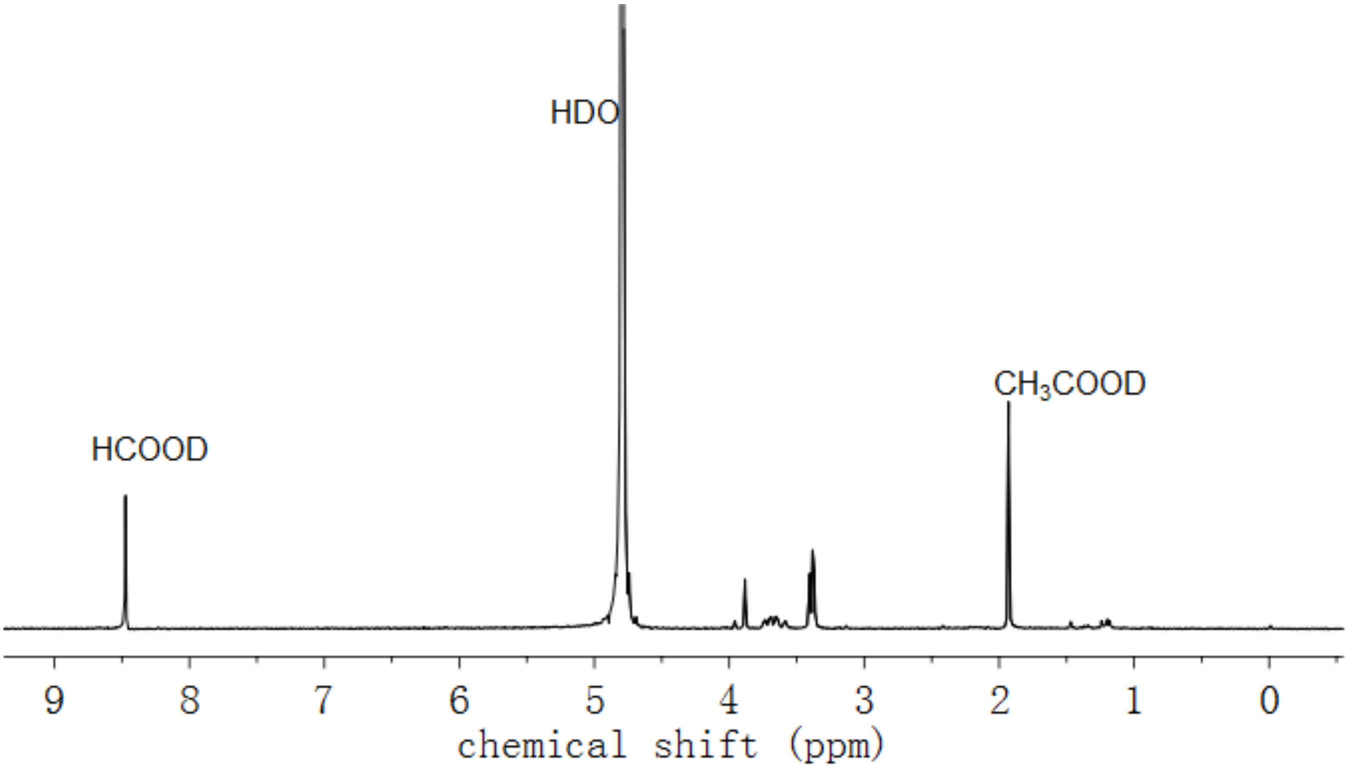

Figure S4. ^{1}H-NMR characterization of discharge side products (0.5 M KPF_6 in butyl diglyme/diglyme as the electrolyte) extracted by D_2O from the carbon electrode. HCOOD (δ=8.47 ppm, singlet) and CH_3COOD (δ=1.93 ppm, singlet) were identified from the NMR spectrum. The other peaks, which could be the combination of the residual solvent and the decomposition products, are not clearly assigned now.

Reference:

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