

Supporting Information

Two birds with one stone: Cu ion redox mediation for non-aqueous Li-O₂ battery

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Experimental Procedures

Cathode preparation: The Ketjenblack (KB, EC600JD, Lion Co. Ltd.) cathodes were prepared by rolling the paste of KB and Polytetrafluoroethylene (suspension, 14%) at a weight ratio of 85:15 and pressing onto the hydrophobic carbon paper. The prepared cathode was cut into plates with a diameter of 7 mm. The mass loading of the cathode is 0.15–1.0 mg·cm⁻². The carbon fiber is directly cut into 7-mm plates for use without other treatment. All the cathode plates were vacuum dried at 90 °C overnight before further fabrication.

Electrolyte preparation: Tetraethylene glycol dimethyl ether (TEGDME) (Sigma Aldrich, >99%) was dried over freshly activated 4 Å molecular sieves for several days. Lithium bis(trifluoromethane) sulfonimide salt (LiTFSI, >98 %, Wako) was used as received. The 1M LiTFSI in TEGDME electrolyte was prepared and stored in a glove box under Ar atmosphere. Copper chloride (CuCl₂) and lithium chloride (LiCl) were vacuum dried overnight before transferred into the glove box. The Cu ion contained electrolyte was prepared by adding certain amounts of CuCl₂ into the prepared 1M LiTFSI electrolyte. The Cu ion concentration was 25 mM, 50 mM and 100 mM, respectively. The electrolyte with chloride only is prepared by adding 100 mM LiCl into the prepared 1M LiTFSI electrolyte.

Anode preparation: Li metal or composite protective layer (CPL) covered Li metal were pressed onto the stainless steel, which served as the current collector. The preparation of the CPL covered Li metal was based on the previous reported method.¹ In a typical process, 0.35 g Al₂O₃, 0.1 g poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP, Mw=455000), 2.0 g N,N-dimethylformamide (DMF) as a solvent and 0.3 g of 1M LiClO₄ in the mixture of ethylene carbonate (EC) and propylene carbonate (PC) (50/50 by volume) electrolyte were mixed to form a gel

electrolyte phase. The CPL covered Li metal was prepared by spreading the as prepared slurry onto the Li metal, followed by vacuum drying at ambient temperature overnight. For the long term cycling test, multiple CPLs covered Li metal was also prepared.

Cell assembly: The cell assemble was conducted in a glove box filled with Ar. 2032-type coin cells with holes on the cathode side were used. Specifically, the Li-O₂ cell was fabricated by successively stacking a Li metal anode, a glassy fiber separator saturated with certain electrolyte and a KB cathode. The prepared cells were sealed in a chamber (650 mL) and the chamber was continuously purged with oxygen for 1 h.

Electrochemical measurements: The galvanostatic electrochemical measurements were carried out on the battery tester system HJ1001SD8 (Hokuto Denko). The cells were discharged and charged at a fixed current and a certain voltage cut-off. For the long term cycling, the specific capacity was fixed at 1000 mAh·g⁻¹ and a current of 500 mA·g⁻¹ based on the cathode loading. Cyclic voltammetry was measured on a Solartron analyzer (SI 1260) at a scan rate of 5 mV·s⁻¹ from 2.0 V to 4.0 V.

Characterizations: For the ex-situ characterization, cells after test were disassembled in the Ar glove box. The cathodes were extracted and washed with DME for several times, followed with vacuum drying for a certain time. The X-ray photoelectron spectroscopy (XPS) spectrum was obtained through a PHI 5000 VersaProbe. The Raman spectra was collected on a JASCO microscope spectrometer (NRS-1000DT). A gas-tight sample holder was used for the test, and a shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) technique was used to evidently enhance the scattering signal.² The Nuclear Magnetic Resonance (NMR) spectra was recorded using a spectrophotometer (500MHz Ultra-Shield™, Bruker). In this case, both cathode

and electrolyte saturated separator are used for test. FTIR measurements were carried out on a FT/IR-6200 spectrometer (JASCO Corp.). The KB cathode on carbon paper was scratched off, then grounded together with dried KBr (Sigma Aldrich) and pressed into hyaline pellets in vacuum under high pressure (4.0 Mpa) for test. The XRD measurement was carried out with a Bruker D8 Advanced diffractometer fitted with Cu-K α X-rays ($\lambda = 1.5406 \text{ \AA}$) radiation. A home-made cell sealed by silicone glue with a Kapton film window was used for test. The SEM images were obtained on a LEO Gemini Supra 35 system. Differential electrochemical mass spectrometry (DEMS) was performed with a home-made Li-O₂ cell. The assembled cells were discharged to a fixed capacity, and then connected onto the mass spectrometer (MS, Clarus@ SQ-8 S, Perkin-Elmer) to quantify the O₂ and CO₂ evolution. Electrochemical quartz crystal microbalance (EQCM) tests were carried out with CHI440C EQCM system (Shanghai Chen Hua Instrument Co., Ltd., P. R. China). The CHI440C connected with high-frequency oscillator was used to control experimental parameters.

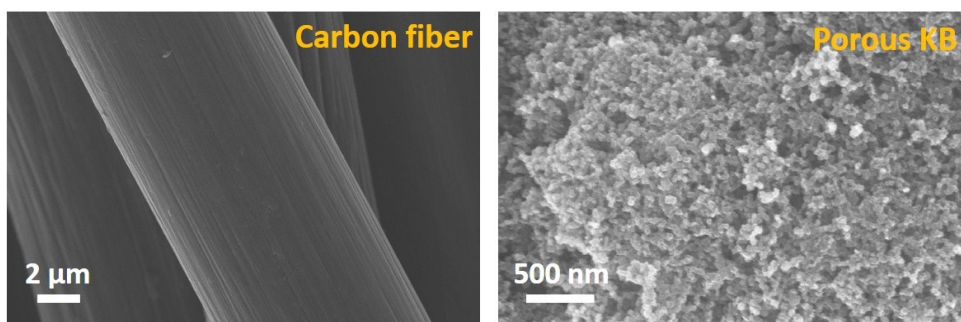


Figure S1. The SEM images of the carbon fiber and Ketjenblack cathodes

The carbon fiber cathode is consisted of fibers with a diameter of several micrometers, while the KB cathode exhibits particles of 50 nm, which construct a porous structure. This is beneficial for the storage of the discharge product Li_2O_2 . Thus the KB cathode shows significantly improved capacity compared with that of the carbon fiber cathode.

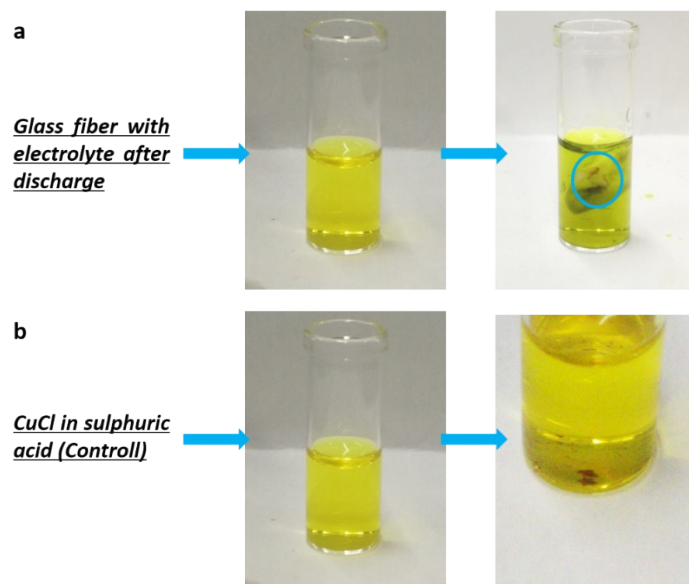


Figure S2. Digital images of the qualitative color reaction. a) test group: glass fibers with Cu ion contained electrolyte after discharge. b) control group: commercial CuCl sample.

In order to confirm the existence of the Cu^+ in the electrolyte during ORR, we take advantage of a kind of method proposed by G. Johar et al., that could identify the Cu^+ through a qualitative color reaction.³ Note that Cu^{2+} would not affect the identification of Cu^+ through this method. Typically, the test material is dissolved by concentrated sulphuric acid, and several drops of this solution are added into the mixture of 1 ml ~10% w/v potassium ferricyanide water solution and 250 μl ammonia solution. The immediate formation of a deep salmon-pink, red-pink, pink-purple or purple color or precipitate indicates the presence of Cu^+ . In our case, as the possible amount of Cu^+ could be very small due to the amount of the electrolyte we use, we prepare two Li-O₂ cells with Cu ion contained electrolyte, and discharge them to 1000 $\text{mAh}\cdot\text{g}^{-1}$. Then, the cells are disassembled and the glass fibers with electrolyte are taken out. We put the two extracted glass fibers into a phial with concentrated sulphuric acid, and then transfer the glass fibers into the potassium ferricyanide/ ammonia solution. As is shown in Fig.

S2, red-pink color immediately appears in the glass fibers after they are immersing in the solution (Fig. S2a). This is in accordance with the control group (Fig. S2b), that we observe a red-pink precipitate when using the CuCl (with Cu⁺) as the test sample. These results strongly indicate the presence of Cu⁺ during the ORR process, corresponding to the CV and our proposed mechanism.

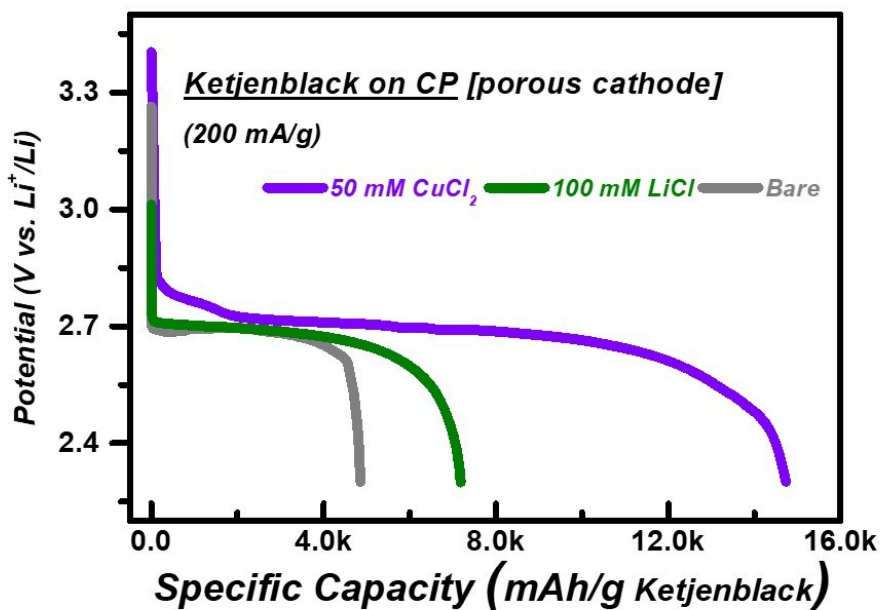


Figure S3. Comparison of the discharge capacity with LiCl and CuCl₂ additives.

The concentration of the chloride ion were controlled to be 100 mM to compare its effect on the improvement of the discharge capacity. With only chloride ion, the discharge capacity is improved to $\sim 7200 \text{ mAh} \cdot \text{g}^{-1}$, due to the chloride ion incorporating into Li₂O₂ crystal to improve its electric conductivity. This is also observed in our SEM mapping and XPS results (Figure S4 and Figure S5). The capacity improvement from the chloride ion alone is quite low compared with that with the Cu ion additive, indicating that the Cu⁺/Cu⁰ redox can enhance the discharge capacity.

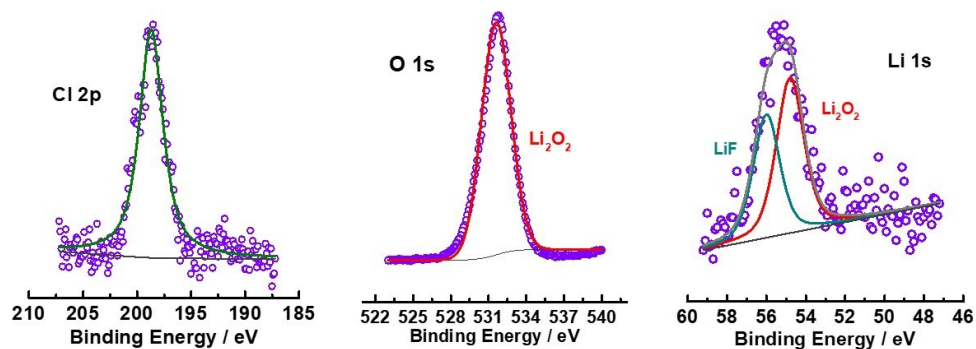


Figure S4. XPS spectrum of the discharged cathode.

The presence of Cl element in the discharged cathode is observed, indicating that chloride ion doping into the discharge product, Li_2O_2 . The presence of Li_2O_2 is confirmed through the O 1s and Li 1s spectra. And we observe some LiF species, which could be related to the LiTFSI decomposition.

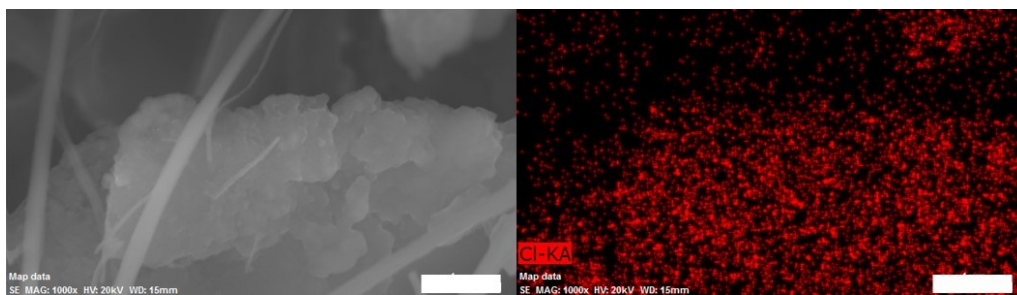


Figure S5. SEM mapping of the Cl element.

The presence of Cl element in the discharged cathode can also be confirmed by the SEM mapping result, which is in accordance with the previous results. Scale Bar: 1 μm .

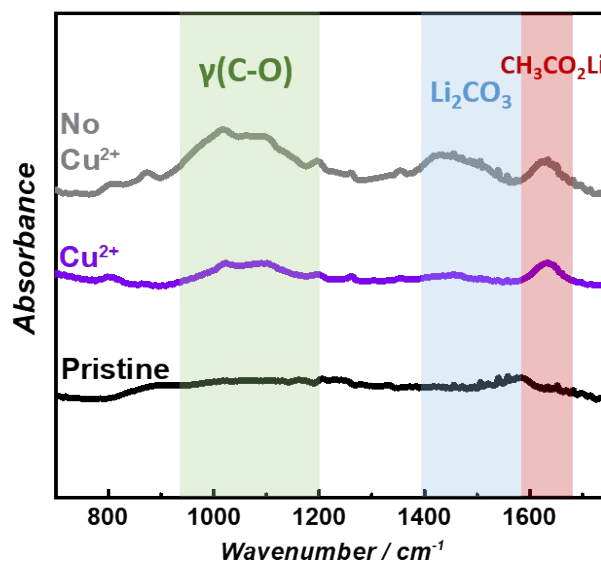


Figure S6. FT-IR spectrum of KB cathode after discharge.

According to the FT-IR results, acetate lithium ($1600\text{ cm}^{-1}\sim 1700\text{ cm}^{-1}$) is detected in both cells with and without Cu ion, while the relative peak intensity of Li_2CO_3 for Cu ion contained Li- O_2 cell is smaller than that of bare electrolyte Li- O_2 cell.⁴ It should be mentioned that the FT-IR results should not be quantitatively analyzed, as we can't exactly control amount of KB sample we used for test. However, we can still observe the relatively weak signal for Li_2CO_3 at the KB cathode of a Cu ion contained cell, which is in accordance with the Raman results, indicating the suppressed parasitic reactions under the function of Cu ion redox

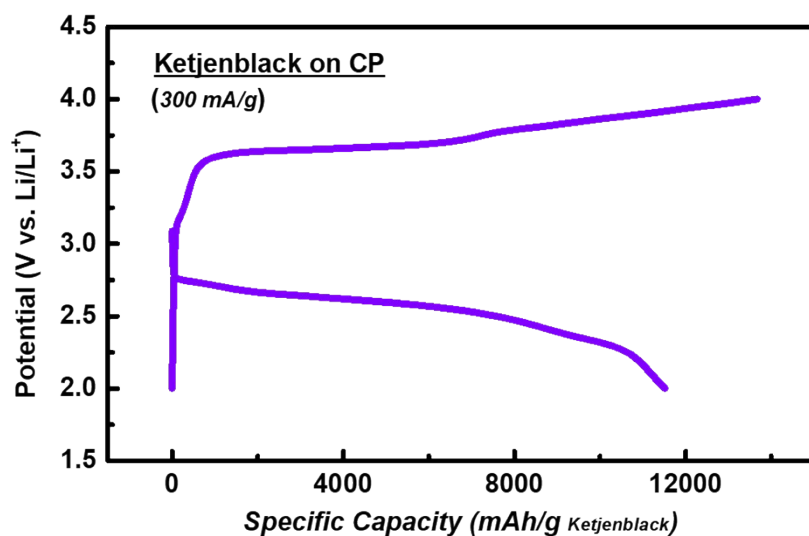


Figure S7. Discharge and recharge profile of Li-O₂ cells with Cu ion RM at KB cathode between 2.0 V~ 4.0 V

A specific capacity of nearly 12000 mAh·g⁻¹ is exhibited at a current of 300 mA·g⁻¹, which is much improved compared with that of a bare electrolyte Li-O₂ battery. Upon recharging, a flat plateau of ~3.6 V is observed at the beginning half part of the charge process, indicating the function of Cu⁺/Cu²⁺ redox. Though the charge potential gradually increases after 7000 mAh·g⁻¹, the total charge process is still controlled below 4.0 V. This is far better than the bare electrolyte Li-O₂ battery, which is hard to recharge under 4.0 V.⁵ These results indicate that the Cu⁺/Cu²⁺ redox participate in the charge process, corresponding with discharge-charge profile at a fixed capacity of 1000 mAh·g⁻¹.

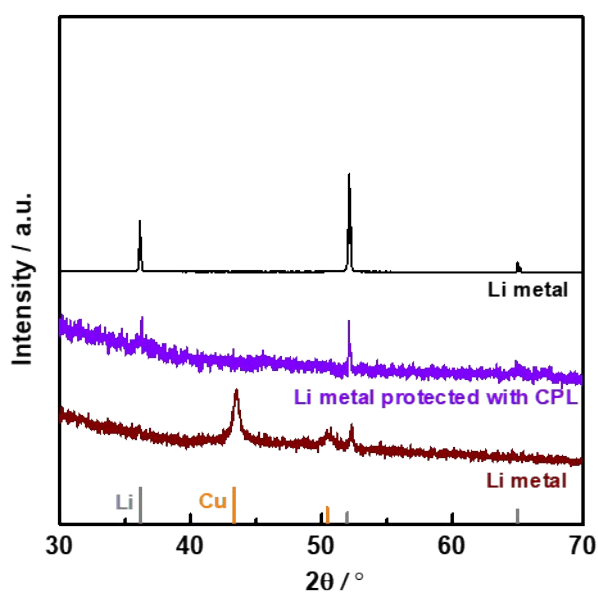


Figure S8. XRD spectrum of Li metal anode with and without CPL covered after contacted with Cu ion contained electrolyte

The Cu ion contained electrolyte was dropped onto the Li metal with or without CPL covered, and kept for 1 hour. Then the Li metal was rinsed with DME solvent, dried, and sealed in an air-tight sample holder for the XRD measurement. The bare Li metal shows strong copper related peaks and significantly weakened Li related peaks, indicating that the Cu ion in the electrolyte was reduced at the surface of the Li metal. In contrast, the Li metal with CPL covered remains the peaks related to Li, and no Cu peaks can be detected. These results show that the CPL can effectively protect the Li metal from reaction with the Cu ion in the electrolyte, which manifests its stability for the long term cycling test.

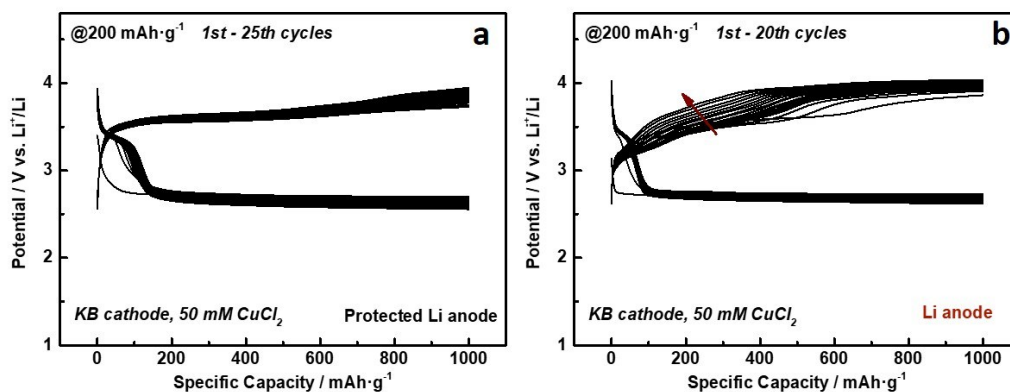


Figure S9. The cycling performance of the Cu ion contained Li-O₂ cells with CPL covered Li metal and bare Li metal.

The electrochemical curves of the Cu ion contained Li-O₂ cells with CPL covered Li metal and bare Li metal are collected at a current density of 200 mA·g⁻¹. The cell with bare Li metal shows low charge potential of ~3.6 V at the first few cycles, indicating the function of the Cu⁺/Cu²⁺ redox in the beginning. However, the charge overpotential gradually increases as the cycles go on, suggesting a continuous reaction of the Cu ion with the Li metal anode, leading to the failure of the Cu⁺/Cu²⁺ redox. This is in contrast with the cell with CPL covered Li anode. A stable and flat charge plateau at ~3.6 V is observed within 25 cycles, indicating the relatively stable function of the Cu ion redox with a CPL covered Li anode.

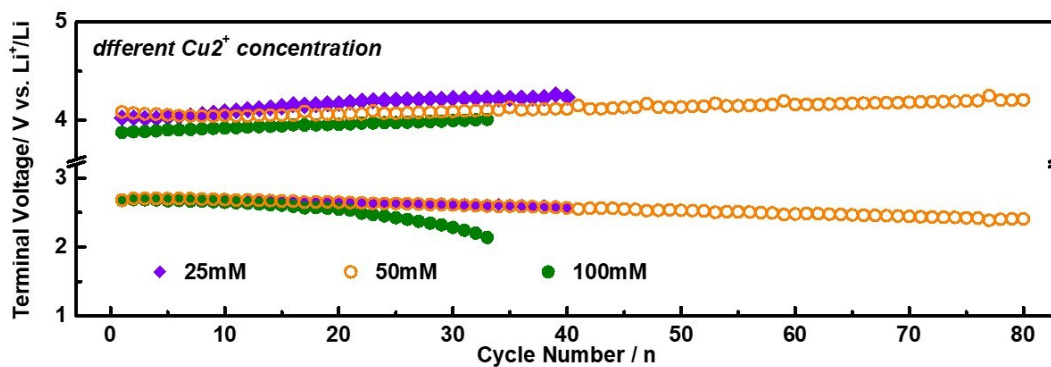


Figure S10. The cycling performances of Li-O₂ cells with different Cu ion concentrations.

The Li-O₂ cells with different Cu ion concentrations are tested for comparison. CPL covered Li anode is used for the test. For all cells, the charge potential is well controlled to ~4.0 V vs. Li⁺/Li. However, for the low Cu ion concentration (25 mM), the charge overpotential increases to a high level after only several cycles. For the high Cu ion concentration (100 mM), while the charge overpotential remains low, the discharge voltage quickly fades, indicating the Li anode corrosion. We thus argue that there exists a trade-off relationship between the overpotential retention and the anode stability that higher Cu ion concentration will promote not only reducing the overpotential but also the anode failure. This again highlights the importance of building a durable protective layer for the RM based Li-O₂ batteries.

References

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Author Contributions

H.D., Y.Q. and H.Z. conceived the concept and designed the experiment. H.D. performed the electrochemical analysis and product characterization. Y.Q. conducted the Raman, DEMS and EQCM analysis. X.Z. performed the EDX mapping experiment. H.D., Y.Q. and H.Z. wrote the paper. All authors discussed the results on the manuscript.