

1 **Supplementary Information**

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3 **Direct cyanation reaction from benzoic acid to benzonitrile**
4 **achieved by paired electrosynthesis in liquid ammonia**

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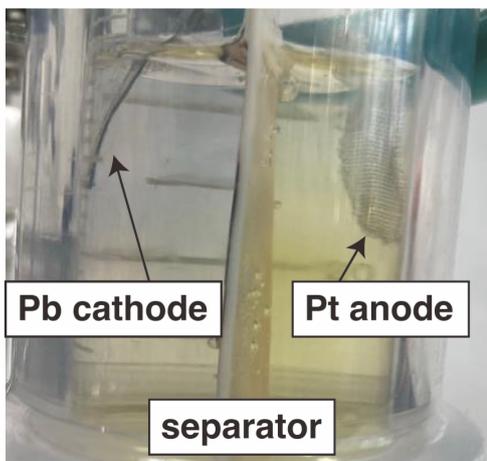
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(a) Benzoic acid + NH₄I



(b) Benzoic acid + KI

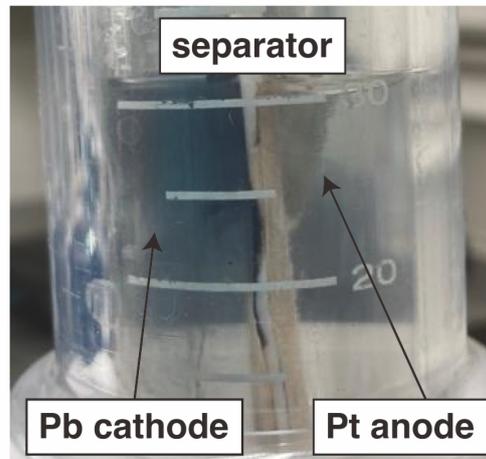


Figure S1 The photographs of the electrochemical cell during the electrolysis in (a) benzoic acid + NH₄I and (b) benzoic acid + KI.

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2 Figure S1(a) shows the color change to yellow at Pt anode, which suggests that I⁻ is
3 electrochemically oxidized to I₂. In the electrolyte of benzoic acid and KI, Pb is dispersed
4 into the electrolyte during the electrolysis. This decomposition of Pb is negligible in the
5 electrolyte of benzoic acid and NH₄I.

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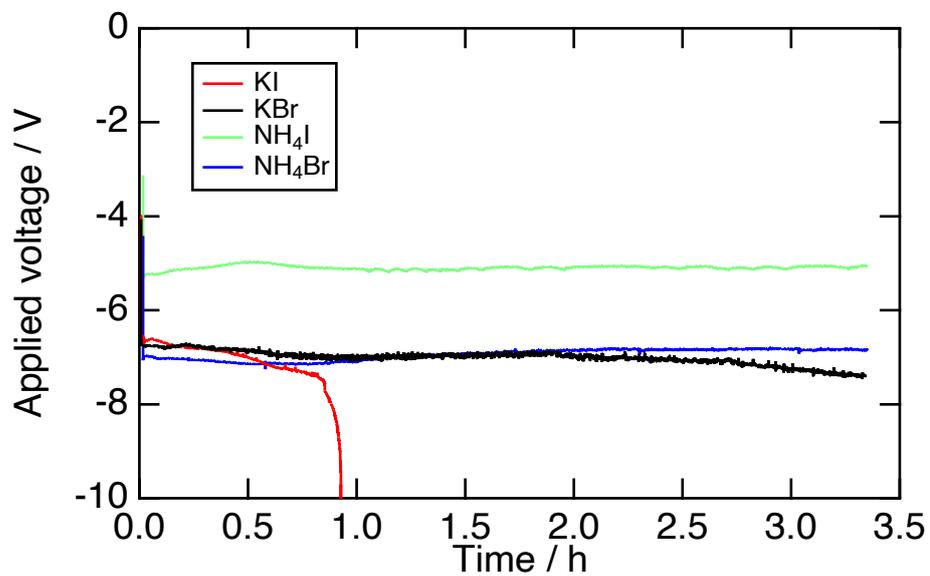


Figure S2 Time dependence of the applied voltage during the constant-current electrolysis of 50 mA in the electrolysis with KI, KBr, NH₄I, NH₄Br. The anode and cathode are Pt mesh and Pb plate, respectively. The applied voltages were stable during the electrolysis. Only in the electrolysis with KI, the electrolysis was abnormally terminated due to the decomposition of Pb electrode.

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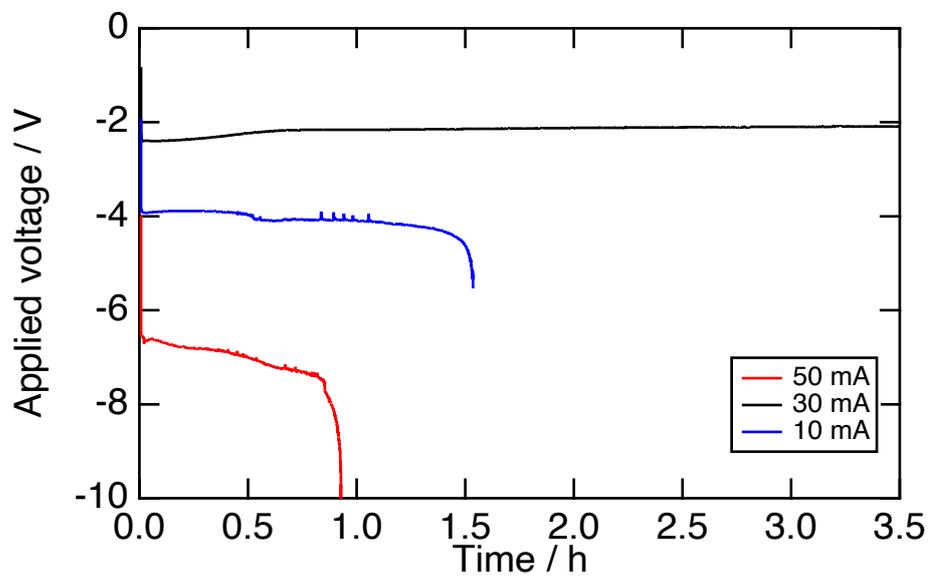


Figure S3 Time dependence of the applied voltage during the constant-current electrolysis of 50, 30, 10 mA. The total charge was 165 C. Pb decomposition occurred in the electrolysis of 50 and 30 mA. In the electrolysis of 50 mA, Pb was completely decomposed, on the other hand, Pb electrode still remained in that of 30 mA.

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