New Systems for the Storage of Electricity using Nitrile and Iodine as the Anodic Active Substances

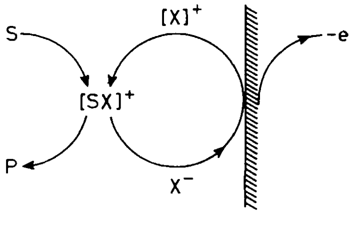
Tatsuya Shono,* Masaya Sawamura, and Shigenori Kashimura

Department of Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo, Kyoto 606, Japan

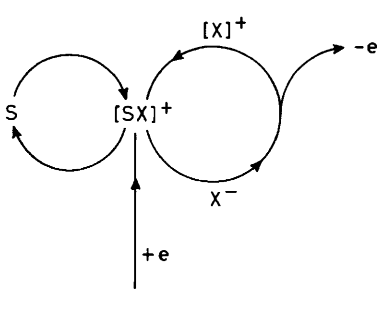
New systems using iodine and nitriles such as acetonitrile and polyacrylonitrile as anodic active substances have been found to be effective for storage of electric energy.

In our continuing study on electro-organic reactions using halogen (Cl, Br, or I) as the mediator,[1] we have found that the oxidized active species of the halogen $[X]^+$ is sufficiently active to interact with compounds S having an electron-donating nature, and the halogen redox system has a sufficiently long life-time.

In usual systems using a mediator, the first intermediate $[SX]^+$ formed through the interaction of $[X]^+$ with S may be rapidly transformed to the product P, and X^- is regenerated



Scheme 1



Scheme 2

$$I_2 \xrightarrow{-2e} 2[I]^+$$

$$[I]^+ + RCN \longrightarrow [RCNI]^+$$

(1)

Scheme 3

Table 1.[a]

$$I_2 \xrightarrow[\text{S, LiBF}_4]{-e,\ (38.6\ \text{C})} (\text{SI})^+\text{BF}_4^-$$

	Terminal voltage		Recovery of electricity	
S	Initial (V_1)	Final (V_2)[b]	Coulomb	%
MeCN	3.65	4.44	29.35	76
DMF	3.39	3.79	18.15	47
DMF–PAN[c]	3.67	3.90	26.98	70
PC	3.67	4.91	8.68	22.5
PhCN	3.54	4.51	22.80	59
Pyridine	3.33	3.70	6.94	18

[a] DMF = dimethylformamide; PAN = polyacrylonitrile; PC = propylene carbonate. [b] 0.2 Faraday/mol of electricity was passed: anode, Pt; cathode, Li/Al; catholyte, PC. [c] PAN was added to the anolyte.

(Scheme 1). On the other hand, when the first intermediate $[\text{SX}]^+$ is sufficiently stable to last for a long period in solution and donation of electrons to $[\text{SX}]^+$ regenerates the starting compounds S and X^- quantitatively, it may be possible for this whole system to be used for the storage of electric energy (Scheme 2). We now report the realization of this possibility.

Since the nature of the electron donor S seems to be an important factor in this system, we have studied the relationship between the structure of S and the efficiency of storage of electric energy. Thus, a solution of iodine (2 mmol) and LiBF_4 (16 mmol) with various donors S (20 ml) was electrolysed in the anodic chamber of a divided cell equipped with a platinum anode (4 cm^2), a lithium cathode (4 cm^2) attached to an aluminium current collector, and a glass diaphragm. The cathodic solution was propylene carbonate (20 ml) containing LiBF_4 (16 mmol) as supporting electrolyte. After 0.2 Faraday/mol of electricity based on the amount of iodine (38.6 C) had passed, the potential between anode and cathode increased from the initial voltage V_1 to V_2 (Table 1). The cell was then discharged from V_2 to V_1 using a load of 10 Ω to measure the efficiency of recovery of electricity.

As shown in Table 1, the recovery of electricity was 76% when S was MeCN (run 1), whereas the use of DMF as S led to only 47% recovery (run 2). Interestingly, the presence of polyacrylonitrile (PAN) in conjunction with DMF led to an increase in recovery (run 3). These results indicate that nitriles such as MeCN and PAN are able to store electric energy by forming stable iodonium ion complexes (**1**) *via* reaction with active iodine species generated by electro-oxidation of iodine.[2]

Using MeCN as S and a load of 400 Ω, charge and discharge were repeated three times, and 86–88% recovery of electricity was observed in each case (current 7.0—8.5 mA). Although our preliminary results with this cell (S = MeCN) are not sufficient for us to discuss its stability as a storage battery, it showed a decrease of 0.3 V in the terminal voltage after 30 h with a load of 1 MΩ. Our results thus strongly suggest that systems using nitrile and iodine as the anodic active substances are highly promising as storage batteries.

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