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Procedia Chemistry 21 (2016) 401 – 408

Procedia Chemistry

5th International ATALANTE Conference on Nuclear Chemistry for Sustainable Fuel Cycles

Cyclic Voltammetry on $CeCl_3$ in LiCl-KCl eutectic using W and Bi Coated Electrode

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Abstract

This paper presents experimental results of cyclic voltammetry on $CeCl_3$ in LiCl-KCl using tungsten electrode and Bi coated electrode respectively at 703 K. Using tungsten electrode at low concentration of $CeCl_3$, the redox reaction has been shown to be reversible. Diffusion coefficient and apparent standard potential of Ce(III) in LiCl-KCl were 0.42×10^{-5} (cm^2/s) and -3.153 (V vs. Cl_2/Cl^-) under 50 mV/s. In order to obtain Bi coated electrode, cyclic voltammetry was carried out on eutectic salt including $BiCl_3$. The redox reaction of Ce on Bi coated electrode has been shown to be reversible and apparent standard potential on Bi coated electrode moved 782 mV compared with tungsten cathode.

Keywords: LiCl-KCl; $CeCl_3$; Cyclic voltammetry; Bi coated electrode; Diffusion coefficient; Apparent standard potential

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1. Introduction

Pyrochemical recycling of spent nuclear fuel has been developed to recover useful resources and separate fission products with proliferation-resistance and accident tolerance. Electrowinning and liquid-liquid extraction processes have become important to co-extract minor actinides for minimizing high level waste in proliferation-resistant manners. Liquid metal cathodes are widely used in the co-extraction processes. Equilibrium reduction potentials of various actinides on liquid metal electrode converge to a narrow enhancing difficulties of pure Pu extraction due to their low activity[1]. While both liquid Cd and liquid Bi support the co-extraction capability, it is reported that

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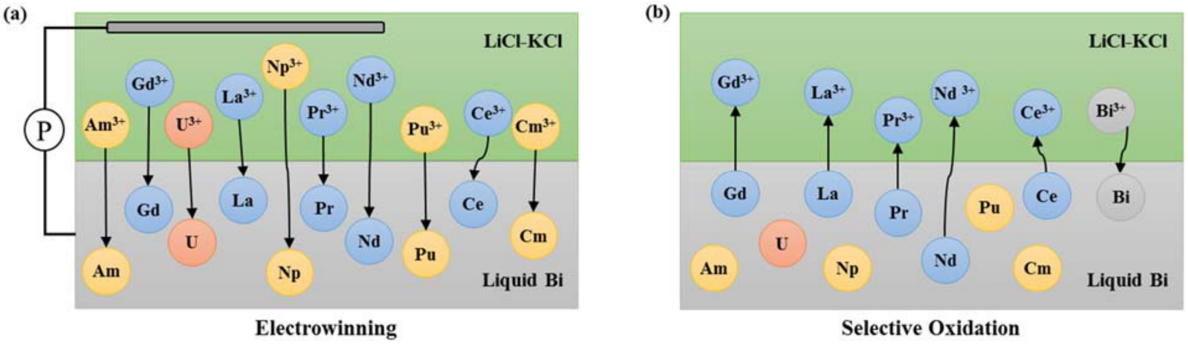
doi:10.1016/j.proche.2016.10.056

liquid bismuth is better than liquid cadmium in terms of lanthanide to actinide separation factor[2].

In order to decontaminate high level waste, PyroRedSox process composed of electrowinning and selective oxidation has been proposed to separate lanthanides from used salt including transuranic elements (TRU) using liquid bismuth and bismuth chloride[3]. In electrowinning, TRU and lanthanides ions in salt are reduced to liquid cathode. Second step is oxidative extraction of reduced lanthanides from liquid metal phase to salt phase by using $BiCl_3$ as an oxidizing agent, as shown in Fig. 1.



Electrowinning

Selective Oxidation

Fig. 1. Concept of PyroRedSox composed of (a) electrowinning and (b) selective oxidation.

During the electrowinning step, cross contamination of lanthanides on TRU is one of the reasons to lower group separation efficiency. Therefore ion behavior on liquid Bi electrode should be investigated. During the selective oxidation step, lanthanides metal preferentially reacts with metal chloride and is oxidized to salt phase due to more negative Gibbs free energy of formation of chloride activities. Therefore molten salt should be continuously monitored on the progress of lanthanides oxidation. This paper presents electrochemical investigation of lanthanides ion on liquid Bi and the applicability of cyclic voltammetry to the lanthanide monitoring in the latter step of PyroRedSox.

Cyclic voltammetry (CV) is used as an experimental technique to examine redox behaviors of Ce ion. From the experiments both thermodynamic and kinetic properties can be measured through identification of reversibility of redox reaction. Earlier experimental investigations showed cyclic voltammetry results on $LiCl\text{-}KCl\text{-}CeCl_3$ with diverse concentrations, scan rates and temperatures to derive diffusion coefficient and apparent standard potential[4, 5, 6, 7]. Also several studies have been performed on cyclic voltammetry of actinides or lanthanides using Bi coated electrode[8, 9, 10]. This study presents cyclic voltammetry (CV) on Ce which is one of the major lanthanides in PWR spent nuclear fuel composition. CV experiments have been conducted for various scan rates using tungsten and Bi coated tungsten as a working electrode so that the effect of liquid bismuth can be determined.

2. Experimental

Electrochemical test were conducted in glove box filled and maintained with argon of 99.999%. Oxygen and moisture concentration were maintained less than 0.5 ppm. Electrochemical cell was set up inside stainless steel furnace which is connected to glove box as represented in Fig. 2. Temperature was maintained as 703 K within ± 2 K using K-type thermocouple and proportional-integral-derivative heater controller.

Working electrode and counter electrode were tungsten wire (Alfa Aesar, 99.95%, d=1mm) with quartz guide tube. Ag/AgCl reference electrode were made of silver wire (Sigma Aldrich, 99.9%, d=1mm) and LiCl-KCl-AgCl (1 wt.%) inserted in a thin Pyrex tube. Anhydrous AgCl (Sigma Aldrich, 99.999%) was prepared for reference electrode. All metal wires were polished by 800 grit SiC paper to remove any impurity. Anhydrous LiCl-KCl eutectic (Sigma Aldrich, 99.99%), $CeCl_3$ (Sigma Aldrich, 99.99%) and $BiCl_3$ (Alfa Aesar, 99.999%) salts were prepared as electrolyte. All electrodes and salts were contained in a quartz cell of 13mm diameter and 45cm height. Electrochemical measurements were carried out using PAR Versastat3 potentiostat with Versastudio software.

Cyclic voltammetry were performed on three kinds of salts, LiCl-KCl-$BiCl_3$ (1 wt.%), LiCl-KCl-$CeCl_3$ (0.456 wt.%), LiCl-KCl-$CeCl_3$ (0.449 wt.%)-$BiCl_3$ (1.522 wt.%). All experiments were performed 24 hours after initial preparation of test cell due to reaching equilibrium of salt and electrode. In order to secure reproducibility of cyclic voltammogram regarding on molten salts containing $BiCl_3$, experiments on each scan rate were performed to measure 30 CV cycles to make stable Bi coated electrode after cleaning and stabilization of open circuit potential.

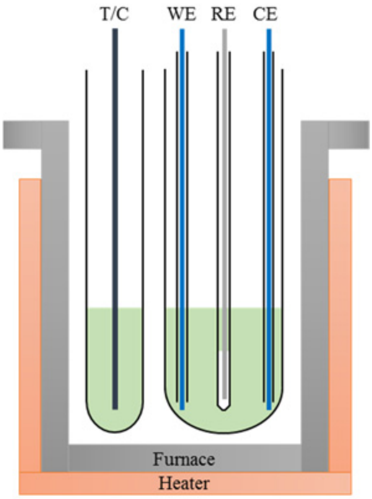


Fig. 2. Electrochemical cell set up for cyclic voltammetry.

3. Results and Discussions

3.1. *Cyclic voltammetry of LiCl-KCl-$CeCl_3$ on W electrode*

Fig. 3 presents cyclic voltammogram measured on LiCl-KCl-$CeCl_3$ (0.456 wt.%) using W electrode for scan range from 0 V to -2.4 V under 50, 100, 200, 300, 400 and 500 mV/s of scan rate at 703K. The surface area of working electrode was 0.848 cm^2. Considering that Li^+ reduction and Cl^- oxidation occurred at approximately – 2.5 V and +1.2 V (vs. Ag/AgCl electrode), redox reaction around 2 V could be attributed to Ce^{3+}. Current between 0.0 V and -2.07 V where Ce^{3+} reaction was occurred is less than 2.5 mA. As scan rate increasing, cathodic and anodic potentials at the highest peak current were maintained as almost same value.

Fig. 4 shows relation between scan rate and peak information to determine reversibility. Compared with horizontal line of -2.1 V in fig. 4(a), there is a slight change of peak potential under various scan rate. Cathodic peak potential difference is 12 mV when scan rate increases from 50 mV/s to 500mV/s. Also there is one linear slope between square root of scan rate and cathodic peak current as shown in Fig. 4(b). These evidences indicate redox reaction of Ce^{3+} at low concentration such as 0.456 wt.% is reversible[11].

For a reversible soluble/insoluble reaction, cathodic peak current is expressed in terms of diffusion coefficient by Berzins-Delahey equation as follows [4]:

$$i_p = 0.611nFAC\sqrt{\frac{nFDv}{RT}} \tag{1}$$

where i_p is cathodic peak current (A), n is number of electron transferred, F is the Faraday constant, A is surface area of working electrode (cm^2), C is molar concentration of species (mol/cm^3), D is diffusion coefficient (cm^2/s), v is scan rate (V/s), R is universal gas constant, T is temperature (K).

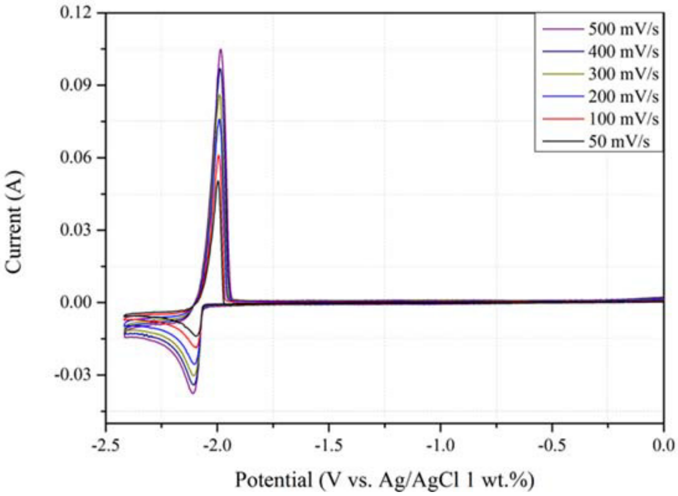


Fig. 3. Cyclic voltammogram of LiCl-KCl-CeCl3 (0.456 wt.%) on W electrode at 703 K

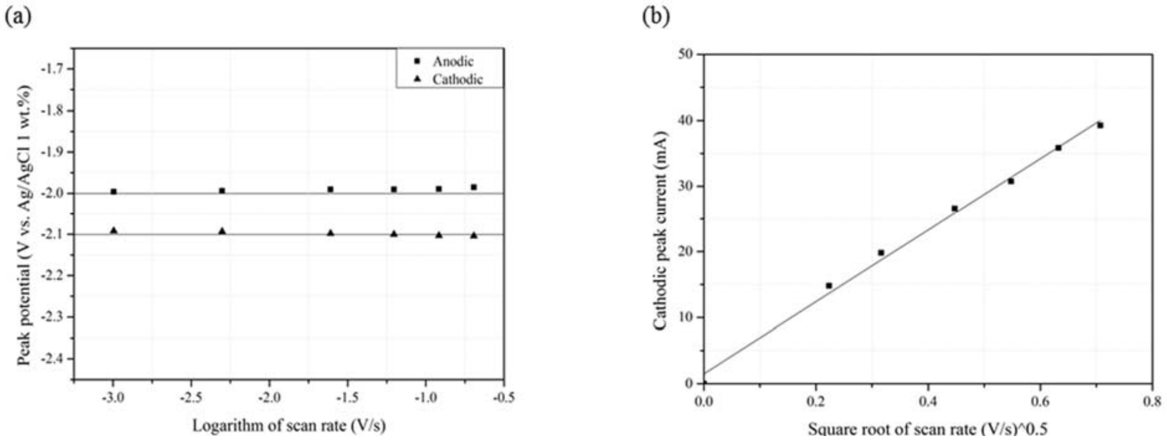


Fig. 4. The relation between scan rate and peak potential and current of CV on LiCl-KCl-CeCl3 (0.456 wt.%); (a) peak potential as a function of the logarithm of scan rate ; (b) the absolute value of cathodic peak current as a function of the square root of scan rate

Table 1 shows diffusion coefficient of Ce^{3+} calculated in this study and other literatures. The derived property has similar value under the change of scan rate. Diffusion coefficient at 50 mV/s is 0.42×10^{-5} cm^2/s and the average value from all the measured results is 0.34×10^{-5} cm^2/s.

For a reversible soluble/insoluble reaction, cathodic peak potential is given in terms of apparent standard potential as follows[12]:

$$E_p = E^{0'} + \frac{RT}{nF} ln(X_{M^{n+}}) - 0.854\frac{RT}{nF} \quad (2)$$

where E_p is cathodic peak potential (V), $E^{0'}$ is apparent standard potential (V), $X_M{}^{n+}$ is mole fraction of M^{n+} in molten salt. Also the difference between Ag/AgCl 1 wt.% reference electrode and Cl_2/Cl^- reference electrode is expressed by[4]

$$E_{AgCl}\ (V) = E^{0'} - 0.9716 - 3.499 \times 10^{-4} T \quad (3)$$

Table 1. Diffusion coefficient of Ce(III) in LiCl-KCl at 703 K

Methods for deriving diffusion coefficient	Concentration of $CeCl_3$	Diffusion coefficient (at T)
Cyclic voltammetry (This study)	0.456 wt.% (3.066×10^{-5} mol/cm^3)	0.42×10^{-5} (50 mV/s, 703 K) 0.34×10^{-5} (Avg. 703 K).
Arrhenius law from experimental data of CV, CP and other literatures[4]	2.88×10^{-4} mol/cm^3	0.87×10^{-5} (703 K)
Cyclic voltammetry[5]	0.5 wt.%	0.479×10^{-5} (698 K)
Arrhenius law from experimental data of CV (Conducted at 833, 863, 893 and 923 K)[6]	1.25×10^{-4} mol/cm^3	1.22×10^{-5} (703 K)
Arrhenius law from experimental data of CV (Conducted at 963 K, 993 K, 1023 K and 1053 K)[7]	2.1×10^{-4} mol/cm^3	0.74×10^{-5} (703 K)

Table 2 shows apparent standard potential of Ce^{3+} calculated in this study and other literatures. As represented in Eq. 3, potential difference between two reference electrodes is -1.2176 V at 703 K. Apparent standard potential has different values as change of scan rate. The maximum value and the minimum value are -3.151 V and -3.163 V respectively and the average value is -3.157 V versus Cl_2/Cl^- electrode.

Table 2. Apparent standard potential of Ce(III) on W cathode in LiCl-KCl at 703 K

Literature	Temperature (K)	Apparent standard potential (V vs. Cl_2/Cl^-)
This study	703	-3.160 (Avg.) -3.153 (50 mV/s)
Mardsen et al.[4]	673	-3.133 (Experiment)
	703	-3.122 (Empirical formula)
Yoon et al.[5]	698	-3.13 ~ -3.17 (Figure)
Zhang et al.[6]	703	-3.120 (Empirical formula)

3.2. Cyclic voltammetry on LiCl-KCl-CeCl$_3$ on Bi coated electrode

In order to investigate the effect of $BiCl_3$, cyclic voltammetry was carried out on LiCl-KCl-$BiCl_3$ using W electrode under 500 mV/s at 703 K. Potential scan started from 0.9 V to -2.7 V. In Fig. 5, Bi^{3+} reduction on W electrode occurred at 0.14 V remarked as R_1. Bi metal was coated onto W electrode. Li+ started to be reduced onto Bi coated electrode at -2.5 V. Reduction peak R_2 at -1.84 V is considered as the deposition of Li on coated Bi and Li-Bi intermetallic is formed [9].

Cyclic voltammetry was performed on LiCl-KCl-$CeCl_3$ (0.449 wt.%)-$BiCl_3$ (1.522 wt.%) using W electrode under 100, 200, 300, 400 and 500 mV/s of scan rate at 703K. Potential scan range was from 0.7 V to -2.4 V to prevent Li^+ reduction and Cl^- oxidation. The surface area of working electrode was 0.848 cm^2 as assuming that thickness of coated Bi is neglected.

Fig. 6 presents cyclic voltammogram including four pairs of redox peak in the total scan range. Concerning redox of Bi onto W electrode and Li onto Bi coated electrode, two pairs of redox peak could be attributed for Ce to react onto Bi coated electrode and form Ce-Bi intermetallic compounds. R_1 and O_1 correspond to redox peak of Bi(III)/Bi(0) shown in Fig. 5 as well. R_2 could be attributed to electrochemical reduction of Ce ion onto Bi coated electrode when it is considered that current was slightly decreased from R_1 at 0.08 V to -1.3 V where reduction of Ce was started. Also there is no peak in this scan range. O_2 was oxidation peak coupled to R_2. It seems that redox reaction of Ce at R_2 and O_2 occurs in Bi rich region. Peak potentials at R_2 and O_2 were almost constant though scan rate was changing. R_3, R_4, O_3 and O_4 could be regarded as redox peak of Li and another redox peak of Ce onto Bi coated electrode, however, no further information could be obtained via cyclic voltammetry.

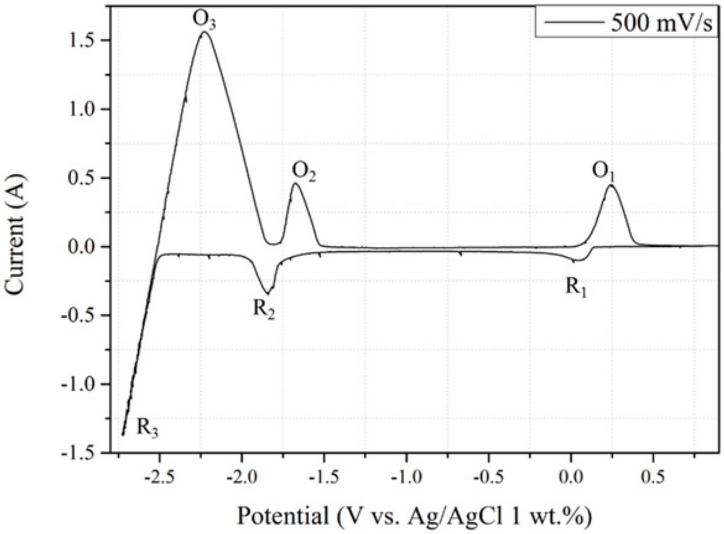


Fig. 5. Cyclic voltammogram of LiCl-KCl-$BiCl_3$ (1 wt.%) on W electrode at 703 K

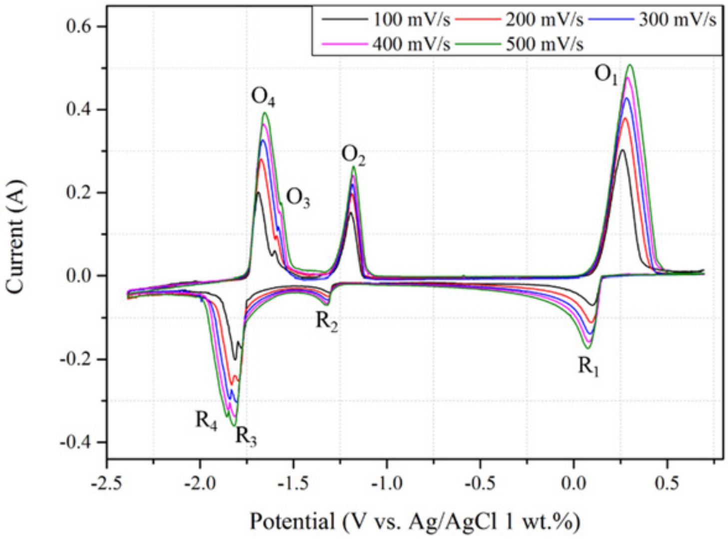


Fig. 6. Cyclic voltammogram of LiCl-KCl-$CeCl_3$ (0.449 wt.%)-$BiCl_3$ (1.522 wt.%) on W electrode at 703 K

Fig. 7 presents relationship between peak potential and peak current versus scan rate to determine reversibility for R_2/O_2. Cathodic and anodic peak potential difference is 12 mV and 16 mV as scan rate increases from 100 mV/s to 500 mV/s in Fig. 7(a). Also there is a linearity with one slope for square root of scan rate as a function of cathodic peak current in Fig. 7(b). This results indicate redox reaction for peak R_2 and O_2 is reversible. Furthermore, those imply that mass transport by diffusion controls the reduction of Ce ion and semi-infinite diffusion model can be applied to the reaction on Bi coated electrode[9]. As represented in Table. 3, apparent standard potential for Ce ion on Bi coated electrode were calculated in the same manner using above Eq. 2 and 3 as above. The potential difference on two electrodes was 0.782 V.

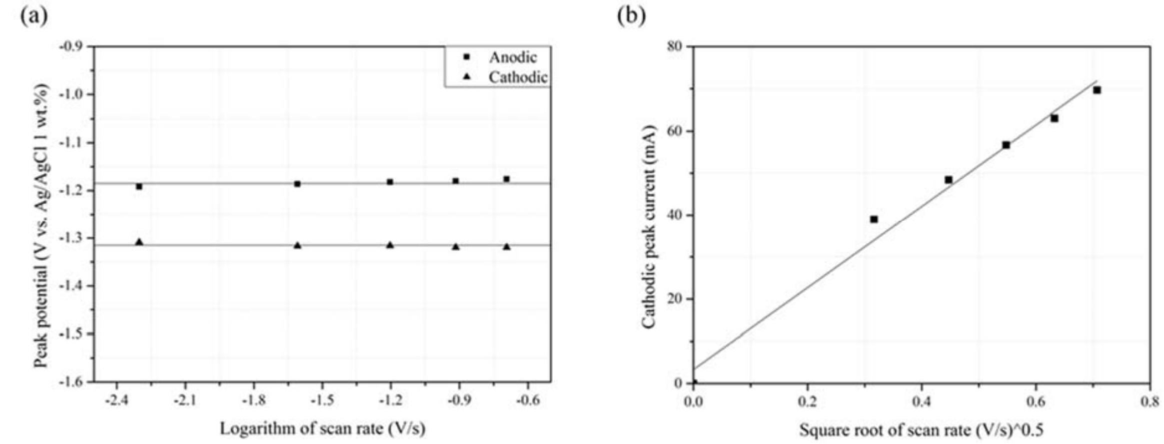


Fig. 7. The relation between scan rate and peak potential and current of CV on LiCl-KCl-$CeCl_3$ (0.449 wt.%)-$BiCl_3$ (1.522 wt.%); (a) peak potential as a function of the logarithm of scan rate ; (b) the absolute value of cathodic peak current as a function of the square root of scan rate

Table 3. Apparent standard potential of Ce on Bi coated electrode at 703 K

	Apparent standard potential (V vs. Cl_2/Cl^-)
Average value	-2.378
Maximum value (At 100 mV/s)	-2.370
Minimum value (At 500 mV/s)	-2.381

4. Conclusions

Electrochemical behavior of Ce in LiCl-KCl eutectic on W and Bi coated electrode has been investigated via cyclic voltammetry. Diffusion coefficient and apparent standard potential were calculated by determining reversibility. The derived properties of Ce ion on W electrode were similar with other literatures. Cyclic voltammogram using Bi coated electrode was performed to obtain the effect of liquid metal electrode and basic information for monitoring selective oxidation. Redox of Ce on Bi coated electrode was reversible and the apparent standard potential is shifted 0.782 V toward to positive direction versus on W electrode. It was observed that another redox reaction of Ce which seems to be irreversible, however, other experimental approaches are needed to determine electrochemical behavior and composition of formed intermetallic compounds.

Acknowledgements

This work was financially supported by the National Research Foundation of Korea (NRF) grant funded by the Ministry of Science, ICT and Future Planning, Republic of Korea (MSIP). (NRF-2011-0031839, NRF-2011-0031890)

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