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<p>(21) International Application Number: PCT/US97/20337 (22) International Filing Date: 4 November 1997 (04.11.97) (30) Priority Data: 08/744,574 6 November 1996 (06.11.96) US (71) Applicant: BOREALIS TECHNICAL LIMITED [US/US]; 23545 N.W. Skyline Boulevard, Hillsboro, OR 97124-9204 (US). (72) Inventor: EDELSON, Jonathan, Sidney; 23545 N.W. Skyline Boulevard, Hillsboro, OR 97124-9204 (US).</p>		<p>(81) Designated States: AL, AT, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i></p>

(54) Title: LOW WORK FUNCTION ELECTRODE

(57) Abstract

A metal surface (1) is coated with a heterocyclic multidentate ligand compound (2), reducing work-function and facilitating the emission of electrons.

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## Low Work Function Electrode.

### Technical Field

The present invention relates to electrodes as used in vacuum electronic systems and structures enabling a current of electrons to flow between a  
5 metallic conductor and another body.

### Background Art

Vacuum electronic devices employ a flow of electrons through a vacuum space between a cathode and an anode. Through manipulation of the voltages of intermediate electrodes, the use of magnetic fields, or other techniques,  
10 various desired end results may be achieved. For example, placing a grid like electrode between cathode and anode permits a small signal applied to said grid to greatly influence the flow of current from cathode to anode: this is the vacuum triode used for amplification. Operation of these devices depends upon the ability of the cathode to emit electrons into the vacuum.

15 Devices employing current flowing through a gas also require electrodes which easily emit electrons. Further, propulsion devices which operate on the principal of current flowing through diffuse plasmas in magnetic fields also depend heavily on the ability of electrodes to easily emit electrons.

Most such devices make use of the heated thermionic cathode. In such a  
20 cathode, a metal or oxide coated metal is heated until thermally excited electrons are capable of escaping from the metal. Such thermionic cathodes are capable of operation at current densities up to several hundreds of amperes per square centimeter. Such devices still find active use in high power devices such as are found in radio transmitters, however at the small  
25 scale the solid state transistor has virtually replaced the vacuum tube in all uses.

A measure of the difficulty of the escape of an electron from an electrode is given by the work function. The work function is the amount of work needed to pull an electron from a bulk neutral material to the vacuum level,  
30 generally measured in electron volts. In a thermionic cathode, this work is supplied by the kinetic energy of the thermally excited electron; rapidly moving electrons are slowed down as they leave the metal, and most electrons do not have sufficient speed to escape and are thus pulled back. However a small fraction of the electrons have enough kinetic energy so as to be able  
35 to escape from the cathode.

The lower the work function of the electrode, the greater the number of electrons which will be capable of escaping from the cathode. If increased current density is not needed, then the lower work function will allow for

operation at lower temperatures. Extremely low work function devices would allow the operation of vacuum electron devices at room temperature, without a heated cathode.

Electrides are organo-metallic compounds comprised of an alkali metal cation, an alkaline earth metal cation, or a lanthanide metal cation, complexed by a multidentate cyclic or poly-cyclic ligand. This ligand so stabilizes the cation that the electron may be considered free from the metal. In solution, electrides consist of the metal-ligand structure in solution as the cation, and free electrons in solution as the anion. Electrides form ionic crystals where the electrons act as the anionic species.

Ligands known to form electrides are cyclic or bicyclic polyethers or polyamines include the crown ethers, cryptands, and aza-crown ethers. Materials which are expected to form electrides include the thio analogs to the crown ethers and the cryptands, as well as the silicon analogs thereto.

In my previous disclosure, entitled "Method and Apparatus for Vacuum Diode-Based Devices with Electride-Coated Electrodes", application number 08/719792, filed 1996 September 25, I describe the use of electride materials to produce electrodes of low work-function for use in vacuum thermionic devices for energy conversion.

In this previous disclosure, I teach the use of bulk electride coatings on conductors. While electrides have demonstrated low temperature thermionic emission, they present several negative attributes. Electrides are thermodynamically unstable, and decompose if not kept at cryogenic temperatures. Electrides also exhibit poor electrical conductivity. In my previous disclosure I specified a new use for the known ability of electrides to thermionically emit electrons.

### Disclosure of Invention

Broadly, the present invention consists of a bulk metal coated with a layer of a complexing ligand capable of forming an electride. The ligand stabilizes the loss of electrons by surface sites on the metal, lowering the work-function of the coated surface. Rather than a thick layer of electride, a thin layer of ligand modifies the electronic structure of the surface of the metal. The bulk metal provides the necessary electrical conductivity. Hot electrons escape the surface, and do not remain to degrade the ligand structure.

In one embodiment of the present invention, said metal is an alkali metal, alkaline earth metal, or lanthanide metal.

In another embodiment, said metal is an alloy comprising a mixture of one or more of alkali metals, alkaline earth metals, lanthanide metals and other metals.

In a further embodiment, the electrider-forming ligand is coated in a monolayer on the metal surface.

In a yet further embodiment, a bulk conductor is plated with a thin layer of alkali metal, alkaline earth metal, or lanthanide metal which is itself  
5 coated with a monolayer of electrider-forming ligand.

It is an object of the present invention to provide for low work function electrodes.

An advantage of the present invention is that lower cathode temperatures may be used in vacuum electron devices.

10 An advantage of the present invention is that unheated cathodes may be used in vacuum electron devices.

An advantage of the present invention is that the efficiency of thermionic converters may be improved.

An advantage of the present invention is that microelectronic thermionic  
15 devices are facilitated.

It is an object of the present invention to provide low work function electrodes which in the main use similar materials to electrodes already in commercial use.

An advantage of the present invention is that it may be integrated into  
20 current production technology.

An advantage of the present invention is that it may be retrofitted into existing products.

## Brief Description of Drawings

### Reference Numerals in Drawings

- 25 1 Metal Electrode
- 1a Conductor
- 1b Metal Layer
- 2 Complexing Ligand

### Description of Drawings

30 Figures 1a and 1b show diagrammatic representations of the low work-function electrode of the present invention.

Figure 2 shows the general chemical structures of some electrider-forming ligand families:

Figure 2a is the general structure of crown ethers.

Figure 2b is the general structure of cryptands.

Figure 2c is the general structure of aza-crown ethers.

Figure 2d is the general structure of silicone crown ethers.

5 Figure 2e is the general structure of thio-crown ethers.

Figure 3 shows the chemical structures of some known electrone forming ligands.

Figure 3a is the structure of 18-crown-6.

10 Figure 3b is the structure of 15-crown-5.

Figure 3c is the structure of cryptand [2.2.2].

Figure 3d is the structure of hexamethyl hexacyclen.

### Best Modes for Carrying Out the Invention

Referring to Figure 1a, metal electrode 1 is coated with a layer of  
15 complexing ligand 2.

In a preferred embodiment, complexing ligand 2 is coated in a monolayer upon the surface of metal electrode 1.

Referring to Figure 1b, conductor 1a is coated first with a layer of metal 1b, forming a composite metal electrode, and secondly, with a layer of  
20 complexing ligand 2.

In a preferred embodiment, metal electrode 1 is composed of an alkali metal, an alloy of alkali metals, or an alloy of alkali metal and other metals. Metal electrode 1 may also consist of an alkaline earth metal, a lanthanide metal, an actinide metal, alloys thereof, or alloys with other metals.

25 In another preferred embodiment, metal electrode 1 is composed of a conducting substrate 1a plated with a metal plating 1b, said metal plating being an alkali metal, an alloy of alkali metals, or an alloy of alkali metal with another metal. Metal plating 1b may also consist of an alkaline earth metal, a lanthanide metal, an actinide metal, alloys thereof, or alloys with  
30 other metals.

The alkali metals are lithium, sodium, potassium, rubidium, cesium, and francium. The alkali earth metals are beryllium, magnesium, calcium,

strontium, barium, and radium. The lanthanide metals are lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, and hafnium. The actinide metals include actinium, thorium, protactinium, uranium, and the transuranic metals.

Referring to figure 2 we see chemical structures for various classes of complexing ligands. Figure 2a is the general structure of the crown-ethers. The crown-ether is a cyclic structure composed of repeated instances of  $\text{CH}_2\text{-CH}_2\text{-O}$ . The oxygen atoms make available non-bonding electron pairs which act to stabilize metal cations. Figure 2b is the general structure of the cryptands. The general structure is a bicyclic poly-ether, composed of repeated instances of  $\text{CH}_2\text{-CH}_2\text{-O}$ , combined with nitrogen 'end-links' which allow for the addition of a third poly-ether chain. Figure 2c is the general structure of the aza-crown-ethers. The aza-crown-ether, or cyclen, is a cyclic structure composed of repeated instances of  $\text{CH}_2\text{-CH}_2\text{-NX}$ , where X is  $\text{CH}_3$ . The nitrogen atoms each make available a single non-bonding electron pair to stabilize metal cations, while being more stable than the oxygen crown-ethers. Figure 2d is a silicone analog to the crown-ethers, a cyclic structure composed of repeated instances of  $\text{Si}(\text{CH}_3)_2\text{-O}$ . Figure 2e is the general structure of the thio-crown-ethers. The thio-crown-ether is a cyclic structure composed of repeated instances of  $\text{CH}_2\text{-CH}_2\text{-S}$ . The sulfur atoms make available non-bonding electron pairs which act to stabilize metal cations.

Referring to figure 3, we see specific examples of complexing ligands known to form electrides and alkalides. Figure 3a is 18-Crown-6, also known by the IUPAC name 1,4,7,10,13,16-hexaoxacyclooctadecane. Figure 3b is 15-Crown-5, also known by the IUPAC name 1,4,7,10,13-pentoxacyclopentadecane. Figure 3c is Cryptand [2,2,2], also known by the IUPAC name 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo [8,8,8] hexacosane.

In a particularly preferred embodiment, metal electrode 1 is composed of nickel substrate 1a, with metal electrode plating 1b being sodium, potassium, francium, or cesium. Layer of complexing ligand 2 is composed of 15-Crown-5 or 18-Crown-6 in a monolayer. Both alkaline plating 1a and crown ether layer 2 may be produced by vacuum sublimation.

In yet another particularly preferred embodiment, metal electrode 1 is composed of nickel substrate 1a, with metal electrode plating 1b being sodium, potassium, francium, or cesium. Layer of complexing ligand 2 is composed of hexamethyl hexacyclen, known by the IUPAC name 1,4,7,10,13,16-hexaaza-1,4,7,10,13,16-hexamethyl cyclooctadecane, in a monolayer. Both alkaline plating 1b and cyclen layer 2 may be produced by vacuum sublimation.

In yet another particularly preferred embodiment, metal electrode 1 is thoriated tungsten. Said cathode is produced in the conventional fashion and baked prior to coating with layer of complexing ligand 2 to ensure a layer of thorium on the surface beneath layer 2.

- 5 In yet another particularly preferred embodiment, metal electrode 1 is carburized thoriated tungsten. Said cathode is produced in the conventional fashion and baked and carburized prior to coating with a layer of complexing ligand 2 to ensure a layer of thorium carbide and tungsten carbide on the surface beneath layer 2.
- 10 In yet another particularly preferred embodiment, metal electrode 1 is cesiated tungsten. Said cathode is produced in the conventional fashion, and processed prior to coating with layer of complexing ligand 2 to ensure a layer of cesium on the surface beneath layer 2.

### Industrial Applicability

- 15 The essence of the present invention is the use of heterocyclic multidentate ligands to stabilize the emission of electrons from a metal. This provides electrodes with low work-function.

Specific metals and ligands have been described, however other metals may be considered, as well as other ligands. For example, stable transition metals  
20 such as copper, gold, or platinum may have there work function reduced sufficiently to be useful.

Although the above specification contains many specificities, these should not be construed as limiting the scope of the invention but as merely providing illustrations of some of the presently preferred embodiments of  
25 this invention. For example, no specification has been given for surface morphology. While the specification is for a layer of ligand upon a surface, this surface may be flat, formed into a shape suitable for a particular application, microstructured to enhance emission using field emission techniques, microstructured to increase surface area, or otherwise altered in  
30 physical configuration.

No specification has been given for electrode size. While large area electrodes such as are used in conventional vacuum tubes, thermionic converters, and the like are facilitated by the present invention, microfabricated vacuum electronic devices are also possible. The present  
35 invention may be used to facilitate the production of flat panel displays, integrated vacuum microcircuits, or vacuum microelectronic mechanical systems.

Thus the scope of the invention should be determined by the appended claims and their legal equivalents, rather than by the examples given.



**Claims**

I claim:

- 1) An electrode having a work function of less than 0.8 eV, comprising
  - a) a metal having a surface and
  - 5 b) a layer of a heterocyclic multidentate ligand coated upon said metal surface.
- 2) The electrode of claim 1 wherein said metal is chosen from the group consisting of the alkali metals, the alkali earth metals, the lanthanide metals, and the actinide metals.
- 10 3) The electrode of claim 1 wherein said metal is an alloy including at least one metal selected from the group consisting of the alkali metals, the alkali earth metals, the lanthanide metals, and the actinide metals.
- 4) The electrode of claim 1 wherein said metal is a layer of less than  
15 one micron in thickness coated upon a conductive body.
- 5) The electrode of claim 1 wherein said heterocyclic multidentate ligand is chosen from the group consisting of the crown-ethers, the cryptands, the aza-crown-ethers, the cyclic-silicones, and the thio-crown-ethers.
- 20 6) The electrode of claim 1 wherein said heterocyclic multidentate ligand is chosen from the group consisting of 15-Crown-5, 18-Crown-6, Cryptand [2.2.2] and hexamethyl hexacyclen.
- 7) The electrode of claim 1 wherein said layer of a heterocyclic multidentate ligand is a monolayer.
- 25 8) An electrode having a work function of less than 0.8 eV, comprising
  - a) nickel having a surface,
  - b) a layer of a second metal coated upon the surface of said nickel, and
  - c) a layer of a heterocyclic multidentate ligand coated in a monolayer  
30 upon the surface of said second metal,whereby the work function of said second metal surface is reduced.
- 9) The electrode of claim 8 wherein said second metal is chosen from the group consisting of the alkali metals, the alkali earth metals, the lanthanide metals, and the actinide metals.
- 35 10) The electrode of claim 8 wherein said heterocyclic multidentate ligand is chosen from the group consisting of the crown-ethers, the cryptands, the aza-crown-ethers, the cyclic-silicones, and the thio-crown-ethers.

- 11) The electrode of claim 8 wherein said heterocyclic multidentate ligand is chosen from the group consisting of 15-Crown-5, 18-Crown-6, Cryptand [2.2.2] and hexamethyl hexacyclen.
- 12) An electrode having a work function of less than 0.8 eV, comprising
- 5 a) a tungsten derivative having a surface and  
b) a layer of a heterocyclic multidentate ligand coated in a monolayer upon the surface of said tungsten derivative,  
whereby the work function of said tungsten derivative surface is reduced.
- 13) The electrode of claim 12 wherein said tungsten derivative is  
10 selected from the group consisting of thoriated tungsten, carburized thoriated tungsten and cesiated tungsten.
- 14) The electrode of claim 12 wherein said heterocyclic multidentate ligand is chosen from the group consisting of the crown-ethers, the cryptands, the aza-crown-ethers, the cyclic-silicones, and the  
15 thio-crown-ethers.
- 15) The electrode of claim 12 wherein said heterocyclic multidentate ligand is chosen from the group consisting of 15-Crown-5, 18-Crown-6, Cryptand [2.2.2] and hexamethyl hexacyclen.

Figure 1a

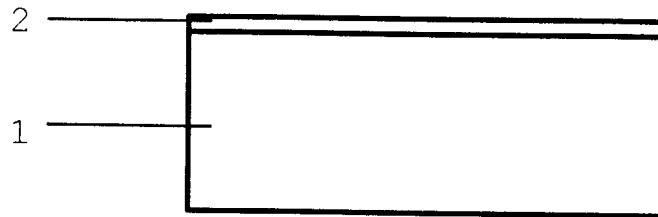
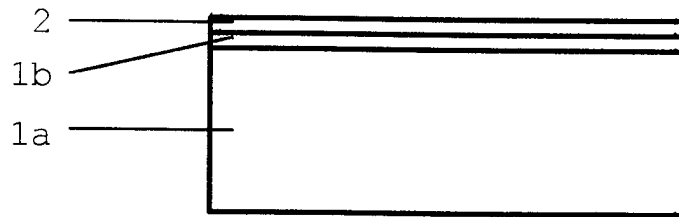


Figure 1b



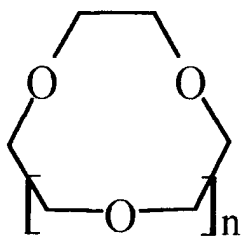


Figure 2a

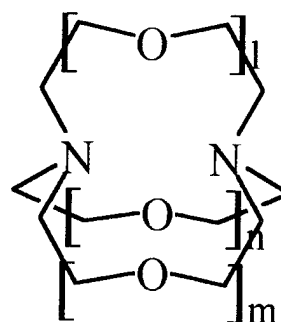


Figure 2b

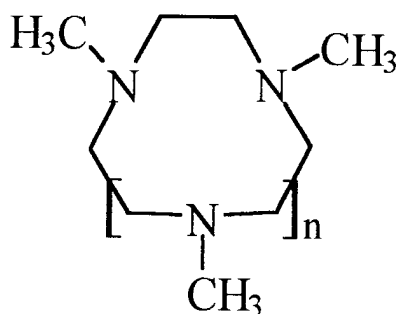


Figure 2c

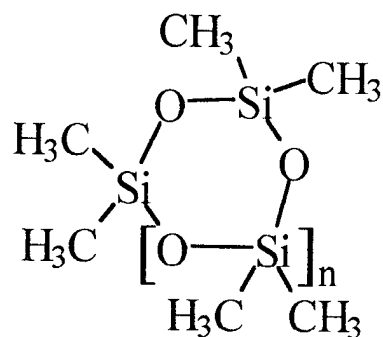


Figure 2d

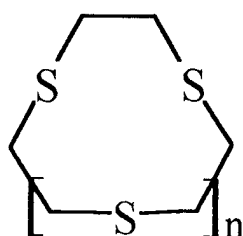


Figure 2e

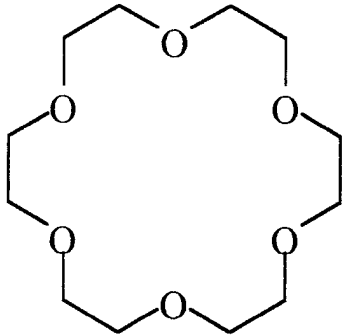


Figure 3a

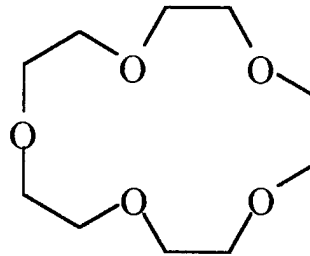


Figure 3b

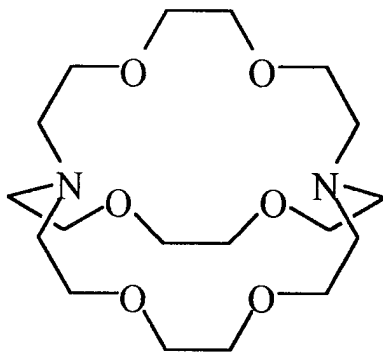


Figure 3c

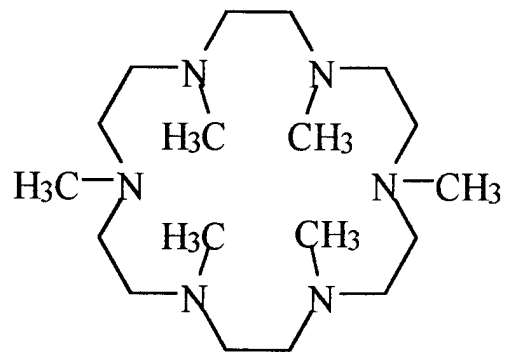


Figure 3d

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/20337

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C25B 11/00, 13/00; G01N 27/26; H01J 1/05  
US CL :204/290R, 290F, 282, 403, 418; 313/310, 311

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Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,484,989 A (MANSELL) 27 November 1984, see col. 2, lines 31-34 and 51-54; col. 3, lines 52-61; col. 5, lines 30-34, 42-44, and 52-61; col. 6, lines 7-45; and col. 7, lines 18-31.	1-11
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Y		12-15
X	US 5,128,587 A (SKOTHEIM et al) 07 July 1992, see col. 2, lines 27-38, 43-47 and 55-58; col. 3, line 35 - col. 4, line 2.	1-5 and 7

Further documents are listed in the continuation of Box C.  See patent family annex.

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