



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>7</sup> : C01D 5/00, 17/00, C01B 13/00, 17/00, 19/00, 25/00, 33/00, H01M 6/18, 8/10, H01B 1/00, G01N 27/406</p>	<p><b>A3</b></p>	<p>(11) International Publication Number: <b>WO 00/45447</b></p> <p>(43) International Publication Date: 3 August 2000 (03.08.00)</p>																		
<p>(21) International Application Number: PCT/US00/01783</p> <p>(22) International Filing Date: 21 January 2000 (21.01.00)</p> <p>(30) Priority Data:</p> <table border="0"> <tr> <td>60/116,741</td> <td>22 January 1999 (22.01.99)</td> <td>US</td> </tr> <tr> <td>60/146,946</td> <td>2 August 1999 (02.08.99)</td> <td>US</td> </tr> <tr> <td>60/146,943</td> <td>2 August 1999 (02.08.99)</td> <td>US</td> </tr> <tr> <td>60/151,811</td> <td>30 August 1999 (30.08.99)</td> <td>US</td> </tr> <tr> <td>09/439,377</td> <td>15 November 1999 (15.11.99)</td> <td>US</td> </tr> </table> <p>(63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application</p> <table border="0"> <tr> <td>US</td> <td>Not furnished (CON)</td> </tr> <tr> <td>Filed on</td> <td>Not furnished</td> </tr> </table> <p>(71) Applicant (for all designated States except US): CALIFORNIA INSTITUTE OF TECHNOLOGY [US/US]; 1200 East California Boulevard, Mail Code 201-85, Pasadena, CA 91125 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): HAILE, Sossina, M. [US/US]; California Institute of Technology, 1200 East California Boulevard, Mail Code 138-78, Pasadena, CA</p>	60/116,741	22 January 1999 (22.01.99)	US	60/146,946	2 August 1999 (02.08.99)	US	60/146,943	2 August 1999 (02.08.99)	US	60/151,811	30 August 1999 (30.08.99)	US	09/439,377	15 November 1999 (15.11.99)	US	US	Not furnished (CON)	Filed on	Not furnished	<p>91125 (US). BOYSEN, Dane [US/US]; California Institute of Technology, 1200 East California Boulevard, Mail Code 178-38, Pasadena, CA 91125 (US). NARAYANAN, Sekharipuram, R. [US/US]; Jet Propulsion Laboratory, 1200 East California Boulevard, Mail Code 277-207, Pasadena, CA 91125 (US). CHISHOLM, Calum [US/US]; California Institute of Technology, 1200 East California Boulevard, Mail Code 198-78, Pasadena, CA 91125 (US).</p> <p>(74) Agent: HARRIS, Scott, C.; Fish &amp; Richardson, P.C., Suite 1400, 4225 Executive Square, La Jolla, CA 92037 (US).</p> <p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p> <p>(88) Date of publication of the international search report: 16 November 2000 (16.11.00)</p>
60/116,741	22 January 1999 (22.01.99)	US																		
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09/439,377	15 November 1999 (15.11.99)	US																		
US	Not furnished (CON)																			
Filed on	Not furnished																			
<p>(54) Title: PROTON CONDUCTING MEMBRANE USING A SOLID ACID</p>																				
<p>(57) Abstract</p> <p>A solid acid material is used as a proton conducting membrane in an electrochemical device. The solid acid material can be one of a plurality of different kinds of materials. A binder can be added, and that binder can be either a nonconducting or a conducting binder. Nonconducting binders can be, for example, a polymer or a glass. A conducting binder enables the device to be both proton conducting and electron conducting.</p> <div data-bbox="877 1299 1388 1814" style="text-align: right;"> </div>																				

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INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/01783

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC(7) :Please See Extra Sheet.  
 US CL :Please See Extra Sheet.  
 According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**  
 Minimum documentation searched (classification system followed by classification symbols)  
 U.S. : 252/184, 500; 429/33, 321; 204/421; 423/305. 326, 508, 512.1, 592, 641

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 USPT, Derwent, EPAB, JPAB, STN Registry, HCAPLUS  
 search terms: Cs, Si, P, S, As, Se, Te, binder, matrix, ceramic, glass, conductive polymer, proton, electron, mixed, conduct\*

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	HAILE, S.M., et al., "X-ray Diffraction Study of Cs <sub>5</sub> (HSO <sub>4</sub> ) <sub>3</sub> (H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> , a New Solid Acid with a Unique Hydrogen-Bond Network", Journal of Solid State Chemistry 140 (2), 1998, pages 251-265, see esp. pages 251 and 252.	1-5, 7-12, 14, 15, 17, 29-32, 67-69, 108-110 ----- 43-62, 65-67, 76-79, 81-85, 87-93, 97, 98

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

• Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search: 29 JULY 2000  
 Date of mailing of the international search report: 17 AUG 2000

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks  
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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/01783

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	OHI, K., et al., "Ferroelectric Phase Transition in Rb <sub>2</sub> SO <sub>4</sub> -(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> and Cs <sub>2</sub> SO <sub>4</sub> -(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> Mixed Crystals", Journal of the Physical Society of Japan 44 (2), February 1978, pages 529-536, see esp. page 529.	1-5, 7, 9, 29-32, 67-69, 108-110 ----- 43-62, 65-67, 76-79, 81-85, 87, 89-93, 97, 98
Y	US 5,573,648 A (SHEN et al) 12 November 1996, see column 11, lines 28-47.	76-82, 84, 85
Y	US 5,591,545 A (MIYASHITA et al) 07 January 1997, see column 7, lines 9-20.	43-49, 51, 52, 58, 60-66, 87-93, 97, 98
Y	US 5,576,115 A (CAPUANO et al) 19 November 1996, see column 2, lines 13-24.	43, 46, 50, 61-66, 97, 98
Y	US 5,436,094 A (HORIMOTO et al) 25 July 1995, see column 4, lines 34-53.	43-49, 52, 59-66
Y	US 5,766,799 A (HONG) 16 June 1998, see column 10, lines 23-50.	43-49, 52-57, 60-67, 76-85, 87, 88, 90-93

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/01783

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	VOLKOV, V. L., et al., "Cesium Ammonium Dihydrogen Arsenate Hydrates", Inorganic Materials (Translation of Neorganicheskie Materialy) 33 (4), April 1997, pages 496-499, see esp. page 496.	1-5, 7, 9, 26, 29-32, 67-69, 108-110 ----- 43-62, 65-67, 76-79, 81-85, 87, 89-93, 97, 98
X -- Y	POLITOVA, T.I., et al., "Ethylene Hydrogenation in Electrochemical Cell with Solid Proton-Conducting Electrolyte", Reaction Kinetics and Catalysis Letters, 41 (2), 1990, pages 321-326, see esp. pages 321 and 322.	1-5, 7, 9, 29-32, 67-69, 108-110 ----- 43-62, 65-67, 76-79, 81-85, 87, 89, 90, 97, 98
X, P ---- Y, P	HAILE, S. M., "Hydrogen-Bonding and Phase Transitions In Proton-Conducting Solid Acids", Mat. Res. Soc. Symp. Proc. 547 (1999), pages 315-326, see esp. page 315.	1-5, 7, 9-11, 13, 14, 17, 26, 29-32, 67-69, 108-110 ----- 43-62, 65-67, 76-79, 81-85, 87-93, 97, 98
X -- Y	MHIRI, T., "Hydrogen Bonding in Cs <sub>1-x</sub> M <sub>x</sub> HSO <sub>4</sub> Protonic Conductors", Solid State Ionics 61 (1-3) 1993, pages 187-191, see esp. page 187.	1-5, 7, 9, 23, 29-32, 67-69, 108-110 ----- 43-62, 65-67, 76-79, 81-85, 87, 89-93, 97, 98
X -- Y	HAILE, S. M., et al., "Superprotonic Conductivity in Cs <sub>3</sub> (HSO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> PO <sub>4</sub> )", Solid State Ionics 77 (1995), pages 128-134, see esp. page 128.	1-5, 7, 9-11, 15, 17, 29-32, 67-69, 108-110 ----- 43-62, 65-67, 76-79, 81-85, 87-93, 97, 98
X -- Y	GARGOURI, M., et al., "Phase Transitions and Electrical Properties of CsH(SO <sub>4</sub> ) <sub>0.76</sub> (SeO <sub>4</sub> ) <sub>0.24</sub> Mixed Crystals", Solid State Ionics 100, 1997, pages 225-232, see esp. page 225.	1-5, 7, 9, 17, 23, 29-32, 67-69, 108-110 ----- 43-62, 65-67, 76-79, 81-85, 87-93, 97, 98

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/01783**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims: it is covered by claims Nos.:  
1-7, 9-15, 17, 18, 23, 24, 26, 29-32, 43-63, 65-69, 76-85, 87-98, 108-110 (specie i, Cs)

**Remark on Protest**

- The additional search fees were accompanied by the applicant's protest.  
 No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/01783

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (7):

CO1D 5/00, 17/00; C01B 13/00, 17/00, 19/00, 25/00, 33/00; H01M 6/18, 8/10; H01B 1/00; G01N 27/406

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

252/184, 500; 429/33, 321; 204/421; 423/305, 326, 508, 512.1, 592, 641

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-32, 43-67 (first occurrence), 67-69, 76-85, 87-98, and 108-110, drawn to a first product of solid acid material.

Group II, claim(s) 33-42, drawn to a first method of use.

Group III, claim(s) 70-75 and 99-107, drawn to a second method of use.

Group IV, claim(s) 86, drawn to a third method of use.

Group V, claim(s) 111, drawn to a fourth method of use.

Group VI, claim(s) 112-115, drawn to a first method of making.

The following species have been identified where M is equal to

- a) Li (claim 23)
- b) Be
- c) Na (claim 24, 96)
- d) Mg
- e) K
- f) Ca (claim 28, 96)
- g) Rb (claim 21, 22, 93)
- h) Sr
- i) Cs (claim 5, 7, 11-15, 17, 18, 23, 24, 26, 36, 62, 87-90, 93, 96, 97, 98)
- j) Ba
- k) Tl (claim 16, 25, 93)
- l) NH<sub>4</sub> (claim 8, 19, 20, 27, 37, 64, 91-93, 96, 97, 98)

Claims 1-4, 6, 9, 10, 29-35, 39-60, 61, 65-68, 69-86, 94, 95, and 99-115 are generic.

The inventions listed as Groups I-VIII do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Regarding Groups II-IV, each is drawn to a method or use or a method of making which do not share a special technical feature which defines a contribution over the prior art (37 C.F.R. 1.475 (a)-(d)).

The separate species outlined above do not share a common core structure, nor is each alternative a recognized equivalent of the other species.